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Project Director: *Makram T. Suidan*

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Office of Water Research & Technology*

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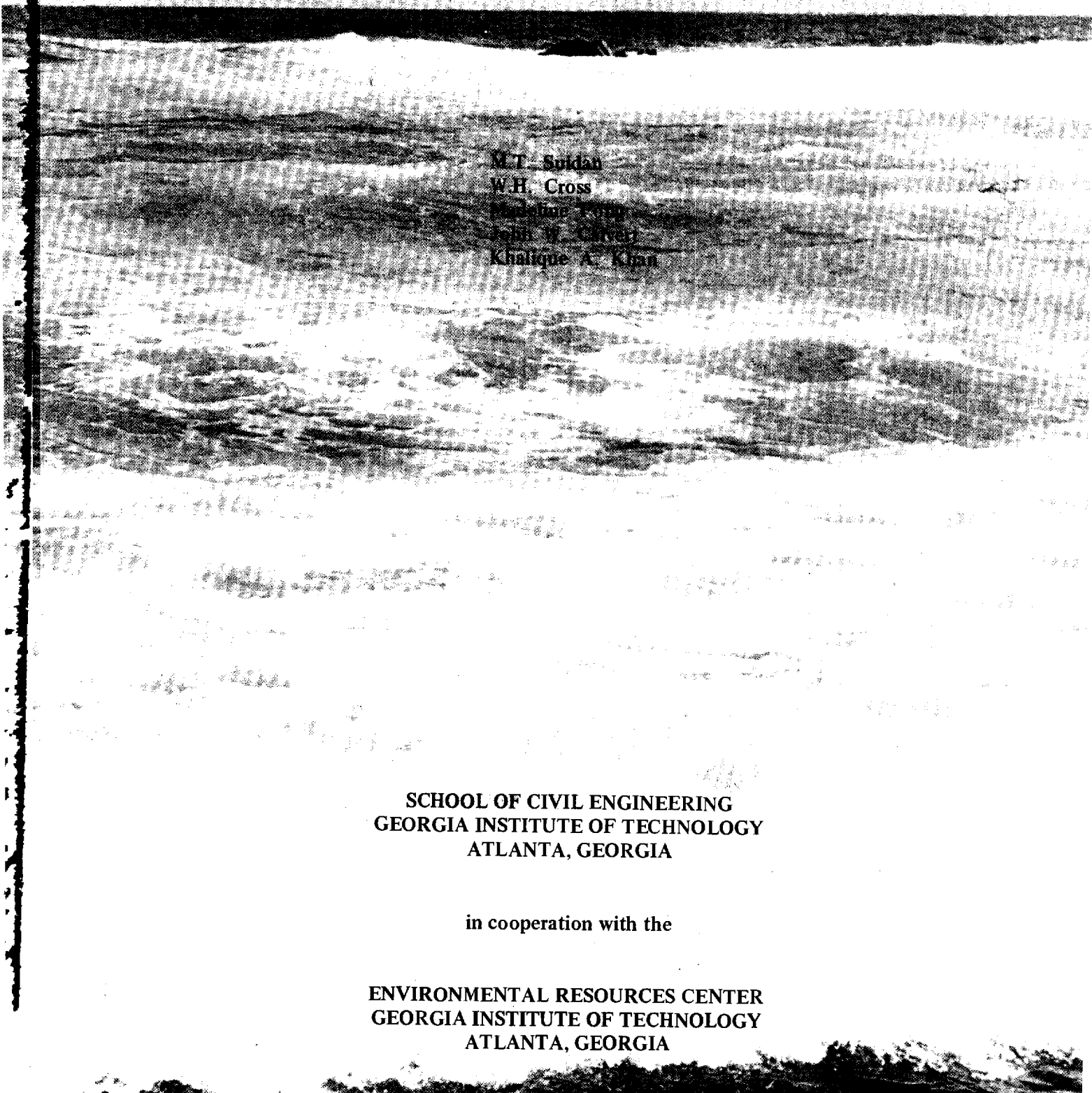
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**ANAEROBIC-ACTIVATED CARBON FILTERS
FOR THE REMOVAL OF REFRACTORY AND
TOXIC ORGANIC COMPOUNDS IN WASTEWATER**



M.T. Soudan
W.H. Cross
M. J. Perry
John W. Garver
Khalique A. Khan

**SCHOOL OF CIVIL ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA**

in cooperation with the

**ENVIRONMENTAL RESOURCES CENTER
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA**

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Madeline Fong
John W. Calvert
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Technical Completion Report
USDI/OWRT Project No. A-077-GA
Initiated October 1977, Completed September 1979

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Report Description

This technical completion report is submitted to the Office of Water Research and Technology in fulfillment of the Reporting Guidelines and contract requirements for USDI/IWRT Allotment Project No. A-077-GA titled Anaerobic-Activated Carbon Filters for the Removal of Refractory and Toxic Organic Compounds in Wastewater. The principal investigators of the project were Drs. Makram T. Suidan and Wendall H. Cross of the School of Civil Engineering, Georgia Institute of Technology.

This report, in part, is the special research problems submitted by Madeline Fong and John W. Calvert in partial fulfillment of the requirements for the M.S.S.E. degree. The special problem research was directed by Drs. Makram T. Suidan and W. H. Cross. The research described in this report represents a portion of an overall effort within the School of Civil Engineering to investigate and design processes for the removal of refractory and toxic organic compounds from wastewater.

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ABSTRACT

The research reported herein involved the development of an effective and energy efficient process for the treatment of phenolic compounds. This process consists of an anaerobic filter with granular activated carbon serving as a media for microbial attachment and substrate concentration and polari-zation.

The anaerobic-activated carbon filter was found very effective in treating a catechol bearing synthetic wastewater. Three feed concentrations of catechol were utilized, 200, 400, and 1000 mg/l and in all instances steady state removal efficiencies ranging from 81 to 94; 88 to 94 and 98 to 99 percent were obtained for total organic carbon, chemical oxygen demand and catechol, respectively. In addition the system proved to be very stable to suddenly increased feed catechol concentrations since instantaneous increases in feed concentrations resulted in increased gas production.

The efficiency of the system in treating an o-cresol bearing synthetic wastewater proved to be limited to adsorption onto the activated carbon packing since no degradation of this aromatic compound seemed to occur.

In a parallel study conducted for the Department of Energy, phenol was found to degrade in a manner very similar to catechol. The results from the two studies seem to confirm that this process, indeed, provides promise for an efficient and energy producing alternative for the treatment of phenol bearing industrial wastewaters.

Suidan, Makram T., Wendall H. Cross, Madeline Fong, John W. Calvert and Khalique A. Khan

ANAEROBIC-ACTIVATED CARBON FILTER FOR THE TREATMENT OF CATECHOL AND O-CRESOL BEARING WASTEWATERS

Final report to the Office of Water Resources Research, Department of the Interior on Annual Allotment Project A-077-GA, September 1979

KEYWORDS: catechol/o-cresol/phenol/anaerobic filter/activated carbon

INTRODUCTION

The general terms "phenols" includes an assortment of organic compounds containing a hydroxyl group plus possibly one or more functional groups attached to an aromatic ring. The presence of phenols in water has special adverse effects. As little as 2 $\mu\text{g}/\text{l}$ of phenol will impart objectionable tastes and odors to drinking water when combined with chlorine to form chlorophenols. Wastewaters containing more than 2 mg/l of phenol are toxic to fish while higher concentrations of phenols in streams may lead to the depletion of the dissolved oxygen content of these streams due to the high oxygen demand of phenol (Rosfjord, 1975; Nebel et al, 1976; Lanouette, 1977). Phenols are also suspected carcinogens and as such they occupy a very important position on the Environmental Protection Agency's Priority Pollutant List.

Sources of phenol discharge to the environment are both natural and industrial in origin. Natural sources of phenol include the urine of some animals and the decay of vegetation (Rosfjord, 1975). Phenols are utilized extensively in manufacturing processes and appear in the liquid wastewaters emanating from the following industries: coal gasification, coking, domestic gas, insulation, leather goods, oil refining, paint and paint stripping, petrochemicals, plastics, pharmaceuticals, plywood manufacturing, pulp and paper mills, textiles and wood preservatives (Rosfjord, 1975; Nebel et al, 1976; Nemerow, 1978).

The major contributors of phenols to the environment are coking plants and oil refineries. Table 1 lists the major industrial contributors of phenols and the corresponding mass concentrations. Coal conversion plants being net consumers of water are also potential polluters. A number of studies have been conducted to determine the nature of the organic constituents of the aqueous by-products of fossil fuel conversion processes (Forney et al.,

1974; Schmidt, 1974; Ho et al., 1976; Klemetson, 1977). The chemical composition of these wastes was found to vary considerably depending on the type of coal used, the process employed, and the operating conditions which include the degree of water recycle (Sack and Bokey, 1978).

In a recent survey aimed at determining the chemical characteristics of coal conversion wastewaters, Singer et al. (1977) concluded that these constituents may be classified into six distinct groups; these were the (a) monohydric phenols, (b) dihydric phenols, (c) polycyclic hydroxy compounds, (d) monocyclic N-aromatics, (e) polycyclic N-aromatics, and (f) aliphatic acids. Table 2 presents a summary of the organic constituents of coal conversion wastewaters and the concentration ranges within which these compounds have been detected.

Table 1
Major Industrial Sources of Phenols
(Ackerman et al., 1977)

Industrial Source	Phenol Concentration Range (mg/l)
Coke Ovens	
before dephenolization	1500-5000
after dephenolization	10-100
Oil Refineries	10-100
Petrochemicals	200-400
Aircraft Maintenance	200-400
Fiberglass Manufacturing	40-400
Plastics	200-600

Table 2. Summary: Organic Constituents in Coal Conversion Wastewaters
(All Concentrations in mg/l)
(Singer, Pfaender, Chinchilli, Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn- thane (3)	COED (4)	SRC (5)	Lurgi- Westfield (6)	Syn- thane (7)	Lurgi- Sasol (8)	Hydro- carboniz. (9)	COED (10)
<u>Monohydric Phenols</u>										
Phenol	1000-4480	10	2100	2100		1250-3100		1250		
o-cresol		30	670	650		153-343	2209	340		
m-cresol	530-3580					170-422		360		
p-cresol		20	1800	1800		160-302		290		
2,6-Xylenol			40	30						
3,5-Xylenol			230	240				50		
2,3-Xylenol			30	40						
2,5-Xylenol	140-1170		250	220		100-393				
3,4-Xylenol			100	900			2185			
2,4-Xylenol			-	-				120		
o-Ethylphenol			30	30						
m-ethylphenol										
p-Ethylphenol										
3-Methyl, 6-Ethylphenol										
2-Methyl, 4-Ethylphenol										
4-Methyl, 2-Ethylphenol	20-150									
5-Methyl, 3-Ethylphenol							66			
2,3,5-Trimethylphenol										
o-Isopropylphenol							40			
<u>Dihydric Phenols</u>										
Catechol						190-555			1700	
3-Methylcatechol						30-394			11	
4-Methylcatechol						110-385				
3,5-Dimethylcatechol										
3,6-Dimethylcatechol						0-45				
Methylpyrocatechol										
Resorcinol						176-272			2000	

Table 2. (continued) Summary: Organic Constituents in Coal Conversion Wastewaters
(All concentrations in mg/l) (Singer, Pfaender, Chinchilli, Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn- thane (3)	COED (4)	SRC (5)	Lurgi- Westfield (6)	Syn- thane (7)	Lurgi- Sasol (8)	Hydro- carboniz. (9)	COED (10)
5-Methylresorcinol						40-64			2000	
4-Methylresorcinol						0-36			2000	
2-Methylresorcinol										
2,4-Dimethylresorcinol										
Hydroquinone									4-7	
<u>Polycyclic Hydroxy Compounds</u>										
γ-Naphthol			10							
β-Naphthol	30-290		30							
Methylnaphthol										
Indenol	20-110									
C ₁ -Indenol										
4-Indanol	40-150						66			
C ₁ -Indanol										
Biphenol	0-110									
<u>Monocyclic N-Aromatics</u>										
Pyridine								117		
Hydroxypyridine									10	
Methylhydroxypyridine									10	
Methylpyridine								104		
Dimethylpyridine	30-580						5	<1		
Ethylpyridine									20	
C ₃ -Pyridine										
C ₄ -Pyridine										
Aniline							21	12		
Methylaniline							9			
Dimethylaniline							11			

Table 2 (continued) Summary: Organic Constituents in Coal Conversion Wastewaters
(All concentrations in mg/l) (Singer, Pfaender, Chinchilli,
Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn- thane (3)	COED (4)	SRC (5)	Lurgi- Westfield (6)	Syn- thane (7)	Lurgi- Sasol (8)	Hydro- Carboniz. (9)	COED (10)
<u>Polycyclic N-Armonatics</u>										
Quinoline							7			
Methylquinoline							27			
Dimethylquinoline										
Ethylquinoline	0-100									
Benzoquinoline										
Methylbenzoquinoline										
Tetrahydroquinoline										
Methyltetrahydroquinoline										
Isoquinoline										
Indole										
Methylindole							63			
Dimethylindole	0-110									
Benzoindole										
Methylbenzoindole										
Carbazole										
Methylcarbazole									4	
Acridine										
Methylacridine										
<u>Aliphatic Acids</u>										
Acetic Acid		600	620	600				171		
Propanoic Acid		210	60	90				26		
n-Butanoic		130	20	40				13		
2-Methylpropanoic Acid		-	-	-				2		
n-Pentanoic Acid		200	10	30				12		
3-Methylbutanoic Acid		-	-	-				1		

Table 2 (continued). Summary: Organic Constituents in Coal Conversion Wastewaters.
(all concentrations in mg/l) (Singer, Pfaender, Chinchilli,
Lamb III, 1977)

	Synthane TPR-86 (1)	Oil Shale (2)	Syn- thane (3)	COED (4)	SRC (5)	Lurgi- Westfield (6)	Syn- thane (7)	Lurgi- Sasol (8)	Hydro- carboniz. (9)	COED (10)
n-Hexanoic Acid		250	20	30						
n-Heptanoic Acid		260	-	-						
n-Octanoic Acid		250	-	-						
n-Nonanoic Acid		100	-	-						
n-Decanoic Acid		50	-	-						
<u>Others</u>										
Benzofurans	10-110									
Benzofuranols	50-100									
Benzothiophenols	10-110									
Acetophenones	90-150									
Hydroxybenzaldehyde or Benzoic Acid	50-110									

LITERATURE REVIEW

The objectives of this research involve the development and testing of an advanced energy efficient and treatment effective process capable of handling phenol bearing wastewaters. This new process consists of an anaerobic biological filter with granular activated carbon serving as a contact medium. Phenol bearing wastewaters have traditionally been treated using either aerobic biological treatment systems or physical chemical processes. Both types of treatment alternatives have proven to be energy intensive as well as requiring close monitoring and control. The intent of the literature review is to provide a comprehensive coverage of the state of the art in the treatment of phenolic wastewaters and to examine the modes of application of activated carbon in the treatment of such wastes. A major emphasis in this review was placed on abstracting what little information is available in the literature on the anaerobic degradation of aromatic compounds.

Treatment of Phenol Bearing Wastewaters - State of the Art

Several technologies have been employed in the treatment of phenol bearing wastewaters. Physical treatment methods include recovery by extraction and incineration, while chemical oxidation methods employ destructive oxidation using powerful oxidants such as chlorine, chlorine dioxide, hydrogen peroxide, ozone and potassium permanganate (Adams, 1974). Phenol bearing wastewaters have also been treated using properly acclimated biological treatment systems such as activated sludge, aerated lagoons, oxidation ponds and oxidation towers.

Phenol Recovery by Solvent Extraction

Solvent extraction processes have been employed for the recovery of phenol in the coal and chemical industries (Adams, 1974). Lanoette (1977)

stated that phenol recovery is economical for wastewater flows exceeding 50 gpm and only when the phenol content of the water is in excess of 2000 mg/l. Patterson (1975), on the other hand, indicated that such technology is economical for wastes containing concentrations of phenol higher than 500 mg/l. A summary by Wurm (1970) of the most commonly used processes for phenol recovery by solvent extraction (Benzene-caustic, Phenolsolvan, and Ifawol dephenolization) is given in Table 3. The benzene-caustic dephenolization process employs benzene as the solvent in conjunction with either a countercurrent packed tower configuration, a Podbielniak centrifugal countercurrent solvent extractor, or in a pulsed packed column. The Phenolsolvan process employs isopropyl ether as the extracting solvent in a multi-stage solvent extractor while in the Ifawol dephenolization process a countercurrent packed column is used in conjunction with a water immiscible solvent having a high boiling point (230-250°C). Although these systems exhibit removal efficiencies as high as 99.7%, significant phenol concentrations remain in the wastewater thus necessitating additional treatment prior to discharge. Volkova et al. (1972) obtained phenol removal efficiencies from a lignite bearing wastewater of 64-90% utilizing a rapid thermolysis process where the extracting solvent was butyl acetate. Testing the effect of ammonia on the phenol extraction process, Volkova et al. (1972) found that at pH values greater than 6, conditions worsen for the recovery of phenol. Wurm (1970) reasserted that further treatment of the wastewater is needed after extraction.

Incineration of Phenolic Wastewaters

Concentrated phenol bearing wastewaters are amenable to treatment by incineration (Adams, 1974). Theoretically, the combustion of phenol to carbon dioxide and water yields a heat of combustion of 13,300 BTU per pound of phenol. Consequently, a mixture of about 18% phenol and 82% water is

Table 3
Methods for the Recovery of Phenols
(Lanouette, 1977)

<u>Process</u>	<u>Extractor Type</u>	<u>Influent Concentration (mg/l)</u>	<u>Removal Efficiency, %</u>
Benzene-Caustic	Packed Column	3,000	92-93
	Podbielniak centrifuge	2,000	95
	Pulsed packed column	2,200-2,600	98.6 - 98.8
Phenolsolvan (low-boiling point solvent)	Multistage	1,570-2,465	99.6 - 99.7
Ifawol (high boiling point solvent)	Packed column	4,000	99

self-sustaining when burnt with 10% excess air at 1400°F (760°C). However, at ambient conditions the solubility of phenol in water is limited to 10% by weight with phase separation occurring at higher phenol contents. In order to maintain an integrated phase, mechanical mixing is required since phase separation may cause the mixture to fall below the phenol content needed for combustion thus entailing the need for supplemental fuel. Ackerman et al. (1977) reported that for a chemical waste composed of 86% water, 5.5% ash and the remaining 8.5% consisting of phenols and cresols, a removal efficiency of 99.999% and a heat content exceeding 1,500 kcal/kg were realized utilizing a fluidized bed operated at an average temperature of 760°C. Problems did occur, however, with probe plugging due to the fracturing and depletion of the reactor bed.

Chemical Oxidation of Phenols

The removal of phenol by chemical oxidation has been primarily practiced either in the treatment of small volumes of concentrated wastes or as a final polishing step for wastewaters containing from 5 to 10 mg/l phenol (Adams, 1974). Chemical oxidation results in the conversion of phenolic compounds to oxidative intermediates; however, at conventional doses of the oxidant the chemical oxygen demand (COD) of the waste is not appreciably reduced rendering additional treatment necessary.

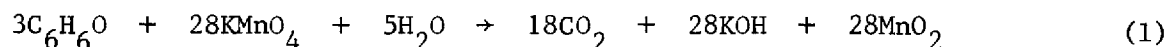
Chlorine is not commonly used as an oxidizing agent because of the potential for forming the more toxic chlorophenols which pose a greater hazard and are less amenable to biological degradation than the parent phenols (Eisenbauer, 1964). Chlorine dioxide has a stronger oxidative capacity than chlorine. This oxidizing agent has been observed to oxidize phenols to benzoquinone in the pH range of 7.0-8.0 and to maleic acid at pH values higher than 10.0 (Adams, 1974).

Hydrogen peroxide in the presence of small quantities of iron salts has been shown to be an effective oxidizing agent for phenols over a wide range of temperatures and concentrations. The optimum pH range for the oxidation of phenol with hydrogen peroxide was found to be from 3 to 5, while outside this range the oxidative power of this reagent is greatly diminished (Eisenbauer, 1964). However, Eisenbauer (1964) observed that when this reagent was applied to certain phenol bearing industrial wastewaters, the hydrogen peroxide requirements were three to six times greater than those needed for synthetic solutions containing equivalent concentration of phenol. This observed difference was attributed to the presence in these wastes of other oxidizable materials which compete with phenol for hydrogen peroxide. In addition, the resulting effluents were highly colored and required precipitation as a post treatment process. At present, the recommended practice has been the addition of this oxidant to equalization basins in order to decrease the phenol concentration thus reducing the probability of shock loading conditions on subsequent biological treatment systems.

Ozonation has been shown to affect substantial reductions in phenol concentrations from water (McKinney et al., 1956; Adams, 1974; Mazur, 1974; Nebel et al., 1976; Gould and Weber, 1976; Capestany et al., 1977; Mueller et al., 1977). Ozone is reported to be twice as powerful an oxidant as hydrogen peroxide; in addition its effective pH range is much wider. Using a refinery effluent, Niegowski (1953) obtained a reduction in phenol concentration from 11,800 mg/l to 2.5 mg/l at an ozone to phenol weight ratio of one. Economically, it has been impractical to ozonate phenol bearing waters to very low levels of phenol due to the high costs associated with attaining low residual levels. A more recent application of ozone has been its application in sufficient doses to oxidize the phenolic compounds to

intermediate organic compounds which are more readily biodegradable (Mueller et al., 1977; Nebel et al., 1976).

Potassium permanganate has been used chiefly in the treatment of paint stripping and foundry wastewaters (Adams, 1974). This oxidant, however, has been noted to constitute an uneconomical additive since 15.7 lb. of KMnO_4 are theoretically required to oxidize one pound of phenol as may be computed from the reaction equation:



Another disadvantage associated with the use of potassium permanganate as an oxidant for phenol is the formation of manganese dioxide which precipitates as a hydrous sludge that must be removed.

Aerobic Treatment of Phenol Bearing Wastewaters

The extended aeration activated sludge process has frequently been used for the treatment of coal conversion and refinery wastewaters (Niegowski, 1953; Nemerow, 1978). McKinney and coworkers (1956) were the first to study the oxidizing capabilities of the activated sludge process in the degradation of phenols. They used synthetic feed solutions of 250 and 500 mg/l phenol and reported removal efficiencies of 39 and 32 percent after twelve hours of aeration. The phenol acclimated culture was also capable of metabolizing catechol, resorcinol, pyrogallol, benzoic acid and benzyl alcohol. Adams (1973) conducted a treatability study on a high strength waste having a phenol content of 3,270 mg/l, a biochemical oxygen demand (BOD) of 6,370 mg/l and a chemical oxygen demand (COD) of 8,230 mg/l, using single and multi-stage activated sludge units. For both process configurations BOD and COD removals of 99 and 97 percent were observed. Capestany et al. (1977) reported COD and BOD removals of 95 percent or better and phenol removals exceeding 99.6 percent from pilot plant and full scale treatment of a high strength

phenolic chemical waste having an influent COD of 4,000 mg/l, BOD of 6,000 mg/l and a phenol concentration of 1000 mg/l. From studies on the activated sludge treatment of a coking plant waste having a strength of 100-1,200 mg/l phenol, 200-400 mg/l thiocyanate, and 200-500 mg/l ammonia, Mazur (1974) observed reductions of 75-85 percent in COD, 90-96 percent in BOD, 50-80 percent in thiocyanate and 20 percent in ammonia. Phenol removals exceeded 99 percent.

Sack and Bokey (1978) and Ganczarczyk and Elion (1978) observed that major organic constituents of coal conversion wastewaters escape treatment in the activated sludge process even when that process is operated at aeration times exceeding six days. Aromatic amines, thiophenes and polycyclic hydrocarbons were found to be specially resistant to aerobic treatment, while the phenolic content of the treated effluent was invariably in excess of desired levels. Other researchers observed that at higher phenol concentrations, the biological culture was more sensitive to temperature, pH and the presence of other compounds in its ability to stabilize phenol (Ackerman, 1977; Sack and Bokey, 1978).

Hubber (1967) studied the effectiveness of a purification scheme consisting of a conventional activated sludge process followed by an aerated lagoon in the treatment of effluents from petrochemical plants and petroleum refineries. The activated sludge portion of the plant was operated with an aeration time of 5-7 hours and a sludge return ratio of 50-100 percent. Hubber found this process configuration to be effective in the biodegradation of the organic content of the wastewaters resulting in appreciable reductions in waste strength as measured by BOD, COD, phenol and total oil. Removal efficiencies of 80-88 percent BOD, 65-80 percent COD, 85-94 percent phenols and 75-85 percent total oils were obtained to produce a final effluent of

15-75 mg/l BOD, 34-56 mg/l COD, 0.05-0.06 mg/l phenol and 1.0-2.0 mg/l total oils. The aerated lagoon was utilized as a final polishing process for the removal of refractory compounds. The removal effectiveness of the lagoon was demonstrated by a 40-80 percent reduction in BOD, 20-46 percent reduction in COD, 50-70 percent reduction in phenol and 40-55 percent reduction in total oils.

In general aerated lagoons, oxidation ponds and oxidation towers have been found to be effective in the treatment of low-strength phenol bearing wastes. Diehl et al. (1970) found aerated lagoons to be successful in removing 99 percent of the phenols present in refinery effluents, thus reducing the effluent phenol content of 0.005-0.05 mg/l. This reduction was affected in an 11 million gallon lagoon, having a surface area of 4 acres mixed with three 75-hp (56 kw) mechanical aerators and having a hydraulic detention time of 6-7 days. Davis et al. (1964) observed in the treatment of refinery wastes with two 2.5 acre ponds operated in series and preceded by pretreatment in an oxidation tower that removal efficiencies exceeding 60 percent COD and 99 percent phenol were possible. The biological oxidation tower, which measured 18 ft. in height and 32.5 ft. in diameter and was packed with high rate corrugated plastic media, was responsible for 50 percent COD removal and 96 percent reduction in phenol.

Aerated lagoons and air or oxygen activated sludge units have been utilized in the treatment of pulp and paper mill wastewaters. Wabers (1978) stated that aerated lagoons and air activated sludge units equipped with primary clarification have the capabilities to remove practically all of the fatty and resin acids, bleach toxicants (chlorinated resin acids, unsaturated fatty acid derivatives, chlorinated phenolics, and halomethanes) and from

79 to 98 percent of the BOD. Typical influent characteristics were 0.73-9.3 mg/l fatty and resin acids, 0.2-1.07 mg/l bleach toxicants and 212-473 mg/l BOD. Feed concentrations of fatty and resin acids exceeding 9.3 mg/l resulted in their reduction by only 69 percent when treated in aerated lagoons. Oxygen-activated sludge systems resulted in only 66 to 77 percent removal for influent fatty and resin acids concentrations of 24.8 and 7.9 mg/l, respectively, while for an influent bleach toxicant concentration of 1.04 mg/l, a removal efficiency of 59 percent was achieved. The oxygen activated sludge process was also capable of producing an effluent COD of 60 mg/l which corresponded to a 90 percent COD removal efficiency (Wabers, 1978). Generally Mueller et al. (1977) have found that aerated lagoons and activated sludge units failed to detoxify bleached kraft mill effluents 15-50 percent of the time. This frequent failure may be due to slug doses from black liquor spills or short-circuiting in the lagoon resulting in incomplete degradation of the toxic compounds. The common deficiencies of these operations include insufficient nitrogen and phosphorus nutrient levels, inadequate oxygen supply, lack of pH control and most importantly, the lack of conditions conducive to the degradation of the compounds by an active microbial culture (Mueller et al., 1977).

Activated Carbon in Biological Wastewater Treatment

An innovative approach to wastewater treatment involves the use of biological-physical-chemical processes. Granular activated carbon adsorption has been employed for tertiary treatment following secondary biological treatment or chemical precipitation. Later technologies have advocated the combination of physical adsorption onto activated carbon with biological degradation in order to produce a cost effective system capable of meeting the more stringent effluent discharge standards.

Granular Activated Carbon

It has long been noted that the surface of activated carbons provide an excellent environment for biological growth. Weber et al. (1972) observed that the adsorptive properties of activated carbon increase the role and extent of concentration of soluble organics at the liquid-solid interface, thereby stimulating bio-growth and assimilation. Characklis (1973) stated that the biofilm on the carbon adhered firmly to the surface where it is sheltered by the pits and crevices of the carbon surface against high velocities. Saunders (1966) stated that an increase in flow velocity resulted in a population density increase in the slime mass. Van Der Kooij (1975) concluded from measurements that under optimum conditions, one bacterium occupies 40 square microns of the activated carbon surface when the total bacterial count was $10^8/\text{cm}^3$. Noting that activated carbons have exceedingly large surface areas, on the order of $1000 \text{ m}^2/\text{gram}$ of carbon, these investigations indicate that high bacterial populations can be supported on activated carbon (Weber, 1972).

Rizzo and Schade (1963), Parkhurst et al. (1967), Bishop et al. (1970), Weber et al (1970) and Tofflemire et al. ((1973) have observed that soluble organic compounds are removed by physical adsorption and anaerobic biological growth. Weber et al. (1972) speculated on a mechanism for the removal of organic compounds, whereby these compounds are first removed by adsorption from the bulk solution onto the carbon surface where they later undergo complete anaerobic decomposition to form low molecular weight organic acids and alcohols. Because of their relatively low adsorption energies, these products diffuse back into the bulk solution. Weber et al. (1972) stated that if the outer film is anaerobic, these products comprise leakage in the effluent while if the outer film is aerobic, these products undergo further

decomposition. No justification was presented by these investigators, however, as to why the organic intermediates would not undergo further anaerobic conversion to methane and carbon dioxide.

Controversy arises as to the benefits of bio-activity on activated carbon. Parkhurst et al. (1976) surmised that the presence of active microorganisms on the carbon surface contributes extensively to the reduction of the organic strength of wastewater. Chian et al. (1975) also stated that acclimated biological growth on activated carbon enhanced the removal of organic matter. Experimentally Weber et al. (1972) have obtained sorption capacities in excess of 60 percent by weight when expressed as organic matter and 90 percent by weight when expressed as COD. Maqsood and Benedek (1977) postulated that anaerobic bio-activity in the form of denitrification occurred in pockets of the anaerobic bed and Weber (1978) attributed BOD and TOC reduction as well as nitrate removal to bio-activity. Basik (1973) found that the concentration of colloidal and dissolved organic matter onto activated carbon to be much higher than that in the aqueous phase thus leading to higher rates of biological BOD removal than were attained in conventional biological processes. In the biological treatment of highly colored textile wastewaters, good color removal was obtained for flow rates of 8.5 and 15.6 gpm/ft² with COD removals of 85 percent and 48 percent for the respective flows (Rodman and Shumney, 1975).

Investigations by Bishop et al. (1970) demonstrated that bio-activity on the activated carbon surface is responsible for the removal of highly water-soluble and poorly adsorbable organic compounds from water; however, because of the coverage of the carbon surface by the biological growth, the rate of physical adsorption was reduced. Eckenfelder et al. (1972) have shown that anaerobic cultures acclimated to the feed waste inhibit carbon

adsorption through surface coverage, however, aerobic cultures with greater bio-activity may or may not enhance carbon adsorption. Overall, research has shown that bio-activity is beneficial if optimum design variables are incorporated into the process.

Parameters of importance in the performance of biologically active carbon are contact time, particle size and density. The level of biological activity is affected by adequate contact time of the soluble organic compounds with the carbon. Shell and Burns (1972) and Sontheimer (1977) state that optimum contact time should be between 15 to 45 minutes (empty bed volume). Moreover, Heukelekian and Crosby (1956) concur that short contact times or high velocities stimulated growth by exposing the biofilm to fresh substrate. Klotz et al. (1975) found that optimum bacterial growth for the degradation of dissolved organic matter within 24 hours while more than 30 days were needed for denitrifying cultures. Weber et al. (1972) believe that an effective acclimation period should extend over several days or weeks in order to provide the microorganisms with sufficient acclimation to biologically resistant substances. The development of the biofilm on the carbon surface allows for that surface to buffer the organisms against shock loads of toxic materials and/or wide variations in waste composition. Magsood and Benedek (1977) agree with these conclusions.

Particle size and density of the carbon play an important role in the operation of these systems. Biological activity is tolerated only in expanded-bed adsorbers where clogging is minimized (Hopkins, 1970; Weber et al., 1972). When biological activity is anticipated, provisions are generally made for either regular backwashing or vigorous air scouring in order to maintain thin biofilm coverage of the carbon thus minimizing transport resistance for the diffusing species. Although particle size has very

little influence on the capacity of carbon for adsorbing solutes, a decrease in particle size results in an increase in external area and, consequently, an increase in solute transport rates and an equivalent increase in surface area available for bio-layer coverage.

One distinct advantage of the biological activated carbon adsorption system is the infrequency of regeneration required of the carbon. Pilot scale carbon adsorption projects at Bremen, West Germany, have been ongoing for three years without any carbon regeneration (Miller and Rice, 1978). At the Rouen water treatment plant on the Seine River in France, carbon adsorption columns have been in operation since January, 1976 without regeneration and removal percentages of 86 ammonia, 87 manganese, 75 detergents, 100 phenols, 75 chloroform extractable compounds and 69 cyclohexane extractable substances have consistently been obtained. Bioactivity at this plant is encouraged through the practice of preozonation. Theoretical modeling has shown that the service life of a carbon is prolonged by biological activity (Maqsoon and Benedek, 1977). Rodman and Shunney (1975) have reported that regeneration of the carbon occurs through desorption followed by biological degradation. Investigations by Johnson (1975) have revealed that bioregeneration effectively maintains the capacity of the carbon very near that of the virgin carbon, thus, this regenerative quality of the biological activated carbon process renders this process very cost effective. Johnson (1975) attributed an appreciable cost reduction to biological activity when larger physical-chemical plants are considered and at least a 50 percent reduction in cost for smaller plants. Weber et al. (1972) and Rodman and Shunney (1975) estimated the cost of biological carbon treatment to be about 8.2¢/1000 gallons.

Addition of Powdered Activated Carbon to Activated Sludge

The concept of adding powdered activated carbon to the activated sludge process was first attempted by Rudolfs and Trubnick in 1935. Their initial investigations led to the conclusion that activated carbon did not facilitate the clarification of the activated sludge process effluent nor did it improve the settleability of the sludge formed. Later research by Adams (1973) demonstrated that the addition of powdered activated carbon to activated sludge will serve to (1) improve the effluent water quality in cases of hydraulic and/or organic overload; (2) enhance the settleability of the solids yielding an easily dewaterable sludge; (3) improve effluent quality by adsorbing toxic or nonbiodegradable substances; (4) minimize effluent operational problems such as foaming and bulking; (5) provide for stable plant operation and consistent effluent quality; (6) increase plant efficiency in a cost effective manner; and (7) eliminate any disposal problems by recovering and regenerating the powdered activated carbon for reuse.

Adams (1973) observed a decrease in effluent COD and BOD levels upon powdered activated carbon addition to full scale activated sludge plants when tested over a wide range of hydraulic and organic loading conditions. The addition of 1000 ppm of powdered activated carbon to a 150,000 gpd activated sludge plant having an influent COD of 3200 ppm and an influent BOD of 1700 ppm resulted in increased removals of 25 percent COD and 20 percent BOD. Robertaccio et al. (1972) obtained reductions in effluent COD values from activated sludge units when powdered activated carbon was added. One possible mechanism responsible for the improved removal of COD and BOD is the adsorption of some of the soluble organic matter onto the carbon. Perrotti and Rodman (1974) demonstrated the synergistic effect of adding powdered activated carbon to the activated sludge process. They noted a twofold increase in TOC removal

during the aerobic oxidation of glucose and phenol. The increased TOC removal far exceeded the adsorptive capacity of the carbon thus lending credibility to the concept of desorption followed by exo-enzyme activity. Ferguson et al. (1976) obtained from batch and continuous testing a decrease in residual COD with increasing carbon dosage. DeWalle et al. (1976) demonstrated that additional COD and BOD removals varied between 5 to 50 percent for powdered activated carbon mixed liquor concentrations of 500 to 7000 ppm. Thus the addition of powdered activated carbon to the activated sludge process contributes to the removal of adsorbable biodegradable organic compounds thereby reducing the oxygen demand in the final effluent.

The mechanisms responsible for the removal of organic and inorganic compounds from wastewater by activated carbon in the activated sludge process are controversial. In literature reviews by Scaramelli and DiGiano (1972), Hals and Benedek (1973) and DeWalle and Chian (1976), citations are made to increased TOC removal as a result of physical adsorption since no changes were observed in oxygen uptake or in the mixed liquor volatile suspended solids concentration. Kalinski (1972) and Koppe et al. (1974), on the other hand, determined experimentally that increased COD removals were due to biological activity since both increased oxygen uptake rates and increased mixed liquor volatile suspended solids concentrations were recorded. Wallace and Burns (1976) stipulated that a biological mechanism was responsible for the removal of 50 percent of the soluble organic compounds. DeWalle et al. (1976) noted that organic carbon removal at low sludge ages is biologically mediated. Earlier in this review, it was stated that the removal mechanism for biological granular activated carbon was a combination of adsorption and biological degradation. Flynn et al. (1976) demonstrated that these mechanisms also hold for powdered carbon addition to activated sludge. They found that

initial removal was due to adsorption alone, however, as the biological activity increases, biological removals followed Monod kinetics and previously occupied adsorptive sites were regenerated. Enhancement of the carbon surface availability by the microbial growth resulted in yet higher organic removal capacities thus indicating that a combination of adsorption and bioregeneration are the prime removal mechanisms in the treatment system.

Important design parameters that must be taken into consideration in dealing with the powdered activated carbon activated sludge system are particle size and density, carbon dose and sludge age. Care is required in selecting a carbon having a particle size exceeding 40 microns in size and having a specific gravity greater than 1.5 in order to affect good solids-water separation (Shell and Burns, 1972). Pilot plant results obtained on the treatment of oil refinery wastewater using a powdered activated carbon activated sludge process showed that high surface area carbons were superior to lower surface area carbons in the treatment of this wastewater (Stenstrum and Grieves, 1977). Flynn et al. (1976) noted that: (1) an increase in sludge age and/or carbon dose improved effluent quality; (2) a high sludge age and a low carbon dose produced an effluent quality similar to the effluent obtained using a low sludge age and a high carbon dose; and (3) the effect of increased sludge age on effluent quality was more apparent with an active biological growth. Ferguson et al. (1976) found that a change in carbon dosage had little effect on effluent quality in the treatment of a biodegradable but non-adsorbable organic compound. Instead they observed that long solids retention times to be desirable in order to allow for the development of diverse and treatment efficient cultures.

Increased sludge age allows for better regeneration of powdered activated carbon. Flynn et al. (1976) stated that complete regeneration was not possible as the microorganisms cannot effectively utilize all the organic

materials adsorbed onto the carbon surface. DeWalle and Chian (1976) found the average COD removal to be generally independent of sludge age. Instead, they observed that biological regeneration to be more a function of biomass to powdered activated carbon concentration, consequently, the potential for bioregeneration increases with decreasing mixed liquor powdered activated carbon concentrations. Moreover, DeWalle and Chian (1976) observed that the biological solids concentration to be dependent on the influent organic strength of the waste, and consequently, they proposed an expression for the daily regeneration capacity $\frac{X}{m\theta_c}$ (mg COD/mg PAC/day) as:

$$\frac{X}{m\theta_c} = k C_o^n \quad (2)$$

where θ_c is the sludge age, C_o is the influent COD concentration, and k and n are constants.

Overall, the addition of powdered activated carbon to the activated sludge process shows great promise for the treatment of moderate to weak soluble organic wastes. Bioregeneration renders this process cost effective since most researchers agree that the mixed liquor carbon concentration rather than the carbon dose represents a control parameter.

Addition of Powdered Activated Carbon to Anaerobic Digesters

Little research has been done on the addition of powdered activated carbon to anaerobic digesters. Rudolfs and Trubnick (1935) demonstrated that activated carbon served to accelerate the digestion of fresh solids, sludges containing toxic materials, and improved digestion at lower than optimum temperatures. Other advantages cited were increased gas production, greater reduction in volatile matter, increased buffering capacity, lower carbon dioxide levels in gas phase, and improved sludge dewaterability.

This work was reinforced by Spencer (1976) who obtained similar results as well as increased methane production. Kornegay and Pohland (1969) proposed the addition of powdered activated carbon to anaerobic digesters which undergo frequent organic overloads. In summary, the adsorptive properties of activated carbon should provide a stabilizing effect for the methanogenic organisms against rapid changes in the environment surrounding them. However, difficulties may arise in the adsorption by the activated carbon of essential growth nutrients as well as in determining the optimum carbon dose that would maximize benefits without limiting the operation of the process.

Biological-physical-chemical treatment is beneficial in the reduction soluble organic and inorganic compounds from water. Experimental findings, thus far, have demonstrated that the use of activated carbon either in a granular columnar configuration or through its addition in the powdered form to disperse growth systems such as the activated sludge process or anaerobic digesters results in improved treatment process performance. Further research is still needed in order to determine the optimum conditions of carbon applications in as far as contact time, particle size and density, carbon dosage and conditions that permit maximum bioregeneration of the carbon.

Degradation of Aromatic Compounds

Anaerobic Degradation of Aromatic Compounds

Tarvin and Buswell (1934) were the first to report on the anaerobic degradation of aromatic compounds by methanogenic bacteria. They investigated the complete destruction and gasification of benzoic, phenylacetic, hydrocinnamic and cinnamic acids (Table 4). The intermediates were analyzed as the lower fatty acids while the final products were carbon dioxide, methane and protoplasm. Some decomposition of o-phthalic acid, salicylic

acid and phenol were noted. Benzyl alcohol was also slightly attacked whereas benzaldehyde, benzene, bromobenzene, toluene and aniline were not.

Clark and Fina (1951) also demonstrated the ability of methanogenic bacteria to degrade benzoic acid anaerobically and utilize it as both a carbon source as well as an energy source. Carbon dioxide and methane were produced after an extremely long acclimation period of approximately 5 weeks. The absence of hydrogen in the gas analyses indicated the possibility of methane being formed by a mechanism other than carbon dioxide reduction. This possibility was contrary to data reported by Stadtman and Baker (1949) and Buswell and Sollo (1948). However, tracer experiments conducted by Clark and Fina showed that very little carbon dioxide was reduced to methane. They concluded that the main source of methane was from the carboxyl carbon.

The investigations of Fina and Fiskin (1960) were directed toward the anaerobic pathway for benzoic acid during methane fermentation. Their tracer studies showed that the second carbon of benzoate was converted to methane with very little of it being oxidized to carbon dioxide. Also, a carbon balance showed that the carbon dioxide, exogenous or from the carboxyl of benzoate, was only partly reduced to methane. Similar conclusions were reached by Roberts (1962).

In another study Clark and Fina (1951) analyzed for the intermediates of the anaerobic decomposition of benzoic acid. Catechol and protocatechnic acid, in quantities equivalent to the carbon of the benzoic acid substrate, were added to two stabilized benzoate-utilizing cultures. The resulting cessation of gas production indicated the failure of the culture to metabolize either of these two compounds under the experimental conditions employed. Thus, the pathway for the anaerobic decomposition of benzoic acid differs from the aerobic pathway suggested by Stadtman and his co-workers (1948, 1950, 1950).

Roberts (1962) in his search for the intermediates formed during the anaerobic decomposition of benzoate found that no lag period existed in the production of methane when cultures acclimated to benzoate were incubated with cyclohexanecarboxylate, butyrate or propionate. However, long periods of induction were required for fumarate, acrylate or 2-methylpropionate. Therefore, he suggested a possible reductive method for the anaerobic degradation of aromatics. Speculation by Evans (1963) based on the isolation of propionate, containing the fourth carbon of the benzene ring but not the first or seventh carbon, from the benzoate culture liquors of experiments performed by Roberts, was that a preliminary saturation of the ring was required prior to its rupture between carbons 1 and 2 and the eventual release of propionate.

Nottingham and Hungate (1969) confirmed the work of Fina and Fiskin (1960) and Roberts (1962) in finding a methanogenic enriched culture from sewage sludges capable of degrading low concentrations of benzoic acid to methane and carbon dioxide under anaerobic conditions.

Others workers have leaned toward the acclimation of a bacterial culture to aromatic compounds under anaerobic conditions. Chimielowski et al. (1964) acclimated a methane fermenting population to phenol as its sole source of carbon. Simpson et al. (1969) demonstrated the ability of a mixed bovine rumen microflora in a synthetic medium to anaerobically degrade phloroglucinol (1,3,5-trihydroxybenzene) at a rapid rate. Tsai and Jones (1975) identified the rumen bacteria to be strains of *Streptococcus bovis*, i.e., Gram-positive coccus. Jeris et al. (1970) reported on the anaerobic digestion of succinic, lactic, glutamic, oleic and benzoic acid in their biochemical studies.

Contrary to past assumptions that conversion of benzoate to methane was accomplished by a single organism, Ferry and Wolfe (1976) presented evidence to show benzoate is converted to methane through a microbial metabolic food chain by a mixed culture composed of nonmethanogenic organisms that degrade benzoate to intermediates which are further metabolized by methanogenic bacteria. Four intermediates were identified: acetate, formate, hydrogen and carbon dioxide. They isolated two methanogenic bacteria, *Methanobacterium formicicum* and *Methanospirillum hungatii*, both strict anaerobes (Ferry et al., 1974) and subjected the bacteria to substrates of formate in one instance and to an atmosphere of 80% hydrogen-20% carbon dioxide. Both subjections yielded methane whereas the substrates tested: acetate, benzoate, ethanol, methanol and pyruvate with the methanogenic bacteria yielded no methane. However, in the mixed bacterial culture, acetate, cyclohexanecarboxylate, 2-hydroxycyclohexanecarboxylate, o-hydroxybenzoic acid, and pimelic acid were converted to methane without a lag. The substrate cyclohex-1-ene-1-carboxylate did not yield methane. Thus Ferry and Wolfe (1976) suggest that a reductive pathway for benzoate exist.

Healy et al. (1977) also found support for a reductive pathway by their aromatic degradation studies. Table 5 lists several aromatic compounds which were found to be acclimated to by a methanogenic enriched culture. Acclimation lag periods were found ranging from 5.5 days to 27 days for syringaldehyde and catechol substrates, respectively. Methane productions were quoted to be 62.4% for phenol, 42% for catechol, 68.2% for vanillic acid and 85.0% for ferulic acid. Healy and Young (1977) stated that the period of acclimation, in particular for catechol, was found to be a function of the source of the seed. They indicated that an acclimation lag of 7 weeks existed before decomposition of catechol was noted.

Table 4
Fermentation of Acids
(32-34°C)
Tarvin and Buswell (1934)

<u>Acid</u>	<u>Grams Carbon in Substrate Feed</u>	<u>Duration (Days)</u>	<u>CO₂</u>	<u>Grams CH₄</u>	<u>Carbon as Protoplasm</u>
Benzoic I (a)	31.2	160	13.58	16.20	0.66
Benzoic II	31.56	130	13.82	16.52	0.98
Phenylacetic	22.50	144	8.16	11.38	0.64
Hydrocinnamic	25.04	135	9.07	13.70	1.40
Cinnamic	35.75	120	15.30	21.15	0.42

(a) incubated at 25-30°C

Table 5
Acclimation Time of Various Substrates
by a Methanogenic Culture
(Healy et al., (1977))

<u>Substrate</u>	<u>Acclimation Lab (Days)</u>	<u>Period of Gas Prod. (Days)</u>	<u>% of Theoretical* Gas Production (Days)</u>
Vanillin	11	29	86
Vanillic Acid	13	27	86
Ferulic Acid	13	28	83
Cinnamic Acid	14	34	80
Benzoic Acid	11	21	84
Catechol	27	12	59
Protocatechuic acid	15	17	74
Phenol	16	21	82
Parahydroxybenzoic Acid	15	17	65.2
Syringic Acid	5.5	14	97
Syringaldehyde	5.5	14.5	100

*Buswell and Sollo eqn. (1948)

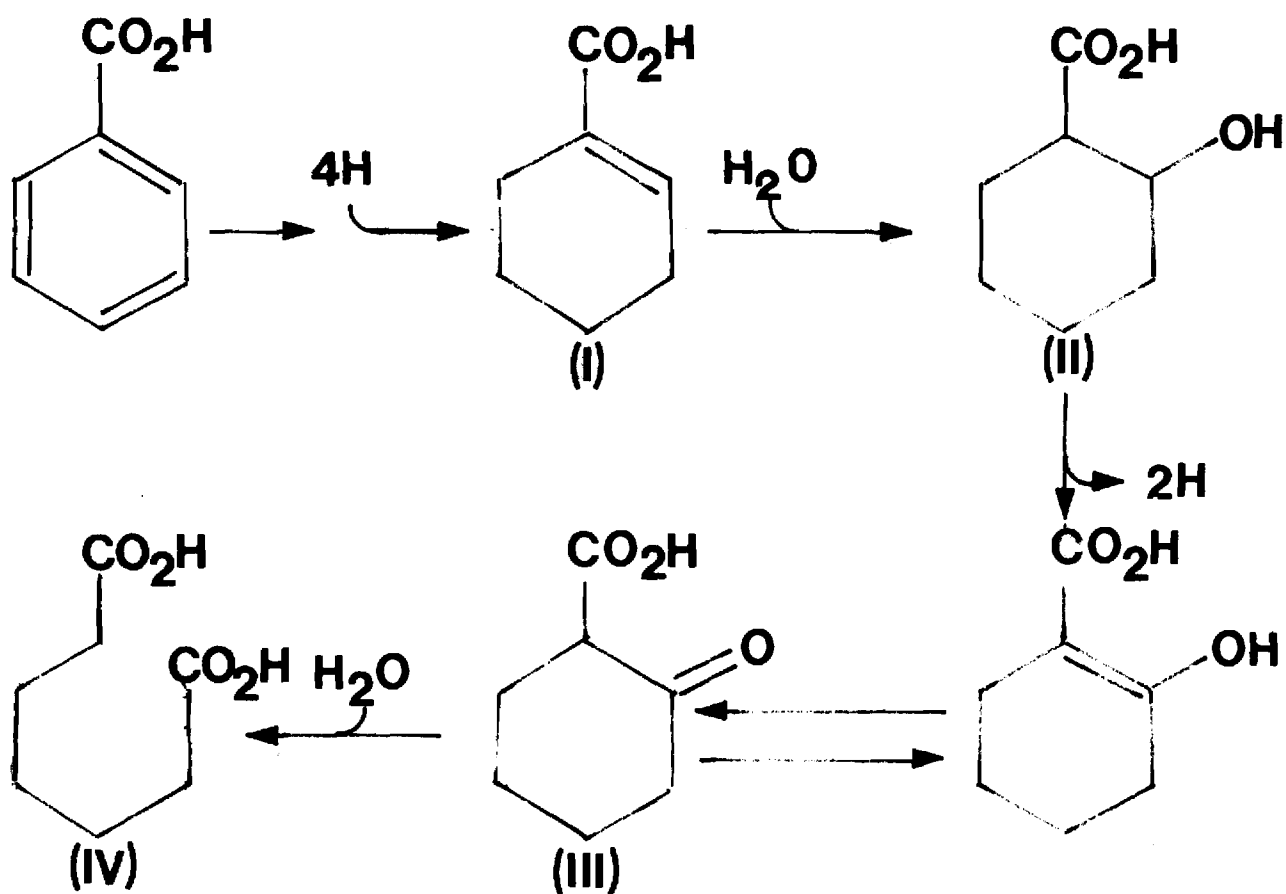
Recent toxicity investigations by Chou et al. (1977) resulted in high levels of degradation for many compounds after a prolonged acclimation period of several months in an anaerobic filter. Among the large number of petrochemicals tested were catechol, resorcinol and nitrobenzene.

Photosynthetic Metabolism Under Anaerobic Conditions

Scher and Proctor (1960) were reportedly the first to successfully isolate strains of non-sulfur photosynthetic bacteria capable of utilizing benzoate anaerobically. Evans (1963) identified these photosynthetic bacteria as *Rhodopseudomonas* and some strains of *Rhodospirillum*. He also determined experimentally that anaerobic photosynthetic degradation exist only if both conditions occurred simultaneously.

Further work done by Dutton and Evans (1969) on the growth kinetics of *Rhodopseudomonas palustris* on the substrates benzoate, m-hydroxybenzoate and p-hydroxybenzoate indicated that the highest growth rate was observed when benzoate was the substrate while the slowest growth rate was when p-hydroxybenzoate was the carbon source. However, *R. palustris* was unable to metabolize o-hydroxybenzoate, protocatechuate or nicotinate under the anaerobic photosynthetic conditions. Isotope-dilution experiments have indicated a reductive pathway for the photometabolism of benzoate by *R. palustris* (Figure 1).

Benzoate is first reduced to cyclohex-1-ene-1-carboxylate (I). Hydration produces 2-hydroxycyclohexane carboxylate (II) which is dehydrogenated to form 2-oxocyclohexane-carboxylate (III). Further hydration results in ring cleavage for the formation of pimelate (IV). In summary, Dutton and Evans concluded that the anaerobic pathway was catalyzed by reductase coupled to a low-redox-potential component of the light-induced electron transport system. The enzymes were found to be inducible and appeared to lack sub-



**PATHWAY PROPOSED FOR THE PHOTOMETABOLISM OF
BENZOIC ACID**

(DUTTON & EVANS, 1969)

FIGURE 1

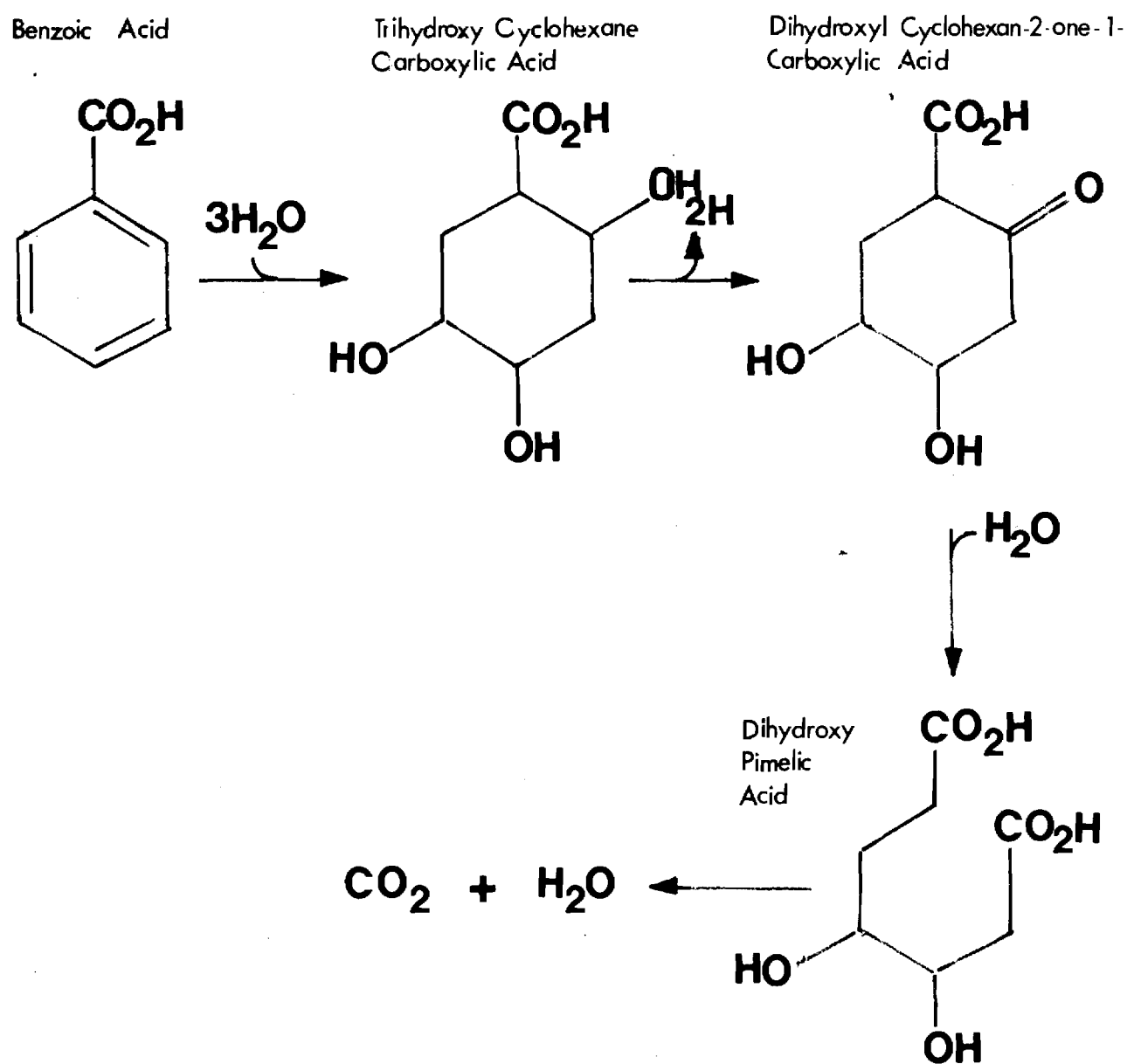
strate specificity. The reduction of the aromatic nucleus to aliphatic cyclic acids was followed by ring fission and subsequent metabolism. Investigations by Guyer and Heyeman (1969) support the reductive pathway proposed by Dutton and Evans (1969) for the anaerobic metabolism of benzoate by *R. palustris*.

Nitrate Respiration Under Anaerobic Conditions

Harary (1956) was the first to isolate an anaerobic spore forming rod, *Clostridium* specie, which was capable of fermenting 6-hydroxynicotinate in the presence of small quantities of yeast extract and peptone. Acetic and propionic acids, carbon dioxide and ammonia were the final products.

Oshima (1965) also reported the ability of mixed cultures of bacteria to grow anaerobically by nitrate respiration on aromatic compounds. It was theorized by Oshima that the oxygen atoms of nitrate are incorporated in a manner similar to the molecular oxygen in the aerobic pathway involving an oxygenase. Thus the possibility arises that certain intermediates are common to both aerobic and anoxic (nitrate respiration) pathways.

Taylor et al. (1970) investigated this mechanism using a pure culture isolated from soil, *Pseudomonas* PN-1. This Gram-negative rod was found capable of growing anaerobically on p-hydroxybenzoate with KNO_3 to yield 4-5 μ moles of nitrogen gas for every μ mole of benzoate. Sixty to seventy percent of the carbon from benzoate was liberated as carbon dioxide. This was an indication of the rupture of the benzene ring. A hypothetical scheme for the anoxic degradation of benzoate was proposed by Taylor et al. (1970) and is depicted in Figure 2. Benzoic acid is first hydrated to trihydroxycyclohexane carboxylic acid. The loss of two atoms of hydrogen results in dihydroxycyclohexan-2-one-1-carboxylic acid, which is later hydrated to dihydroxy pimelic acid thus indicating cleavage of the benzene ring. This is similar to the reductive mechanism suggested by Dutton and



**PROPOSED PATHWAY FOR ANAEROBIC DEGRADATION
OF BENZOIC ACID
(TAYLOR, CAMPBELL, & CHINYOY, 1970)
FIGURE 2**

Evans (1969), but is borrowed from the aerobic pathway for metabolism of aromatic compounds as proposed by Stanier (1948).

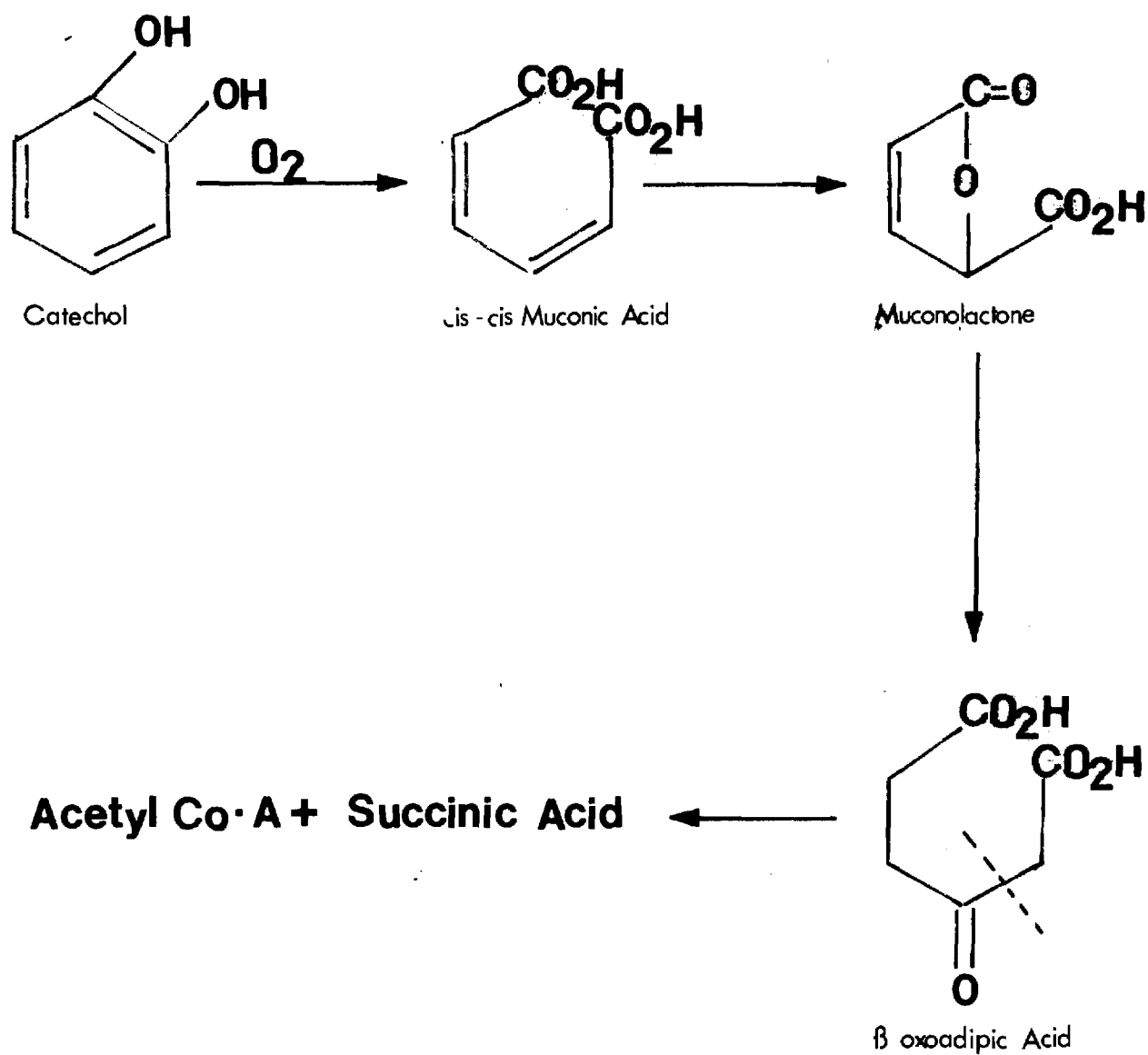
Williams and Evans (1973) reaffirmed the work of Taylor et al. (1970). Pursuing the topic, Williams and Evans (1975) isolated a *Moraxella* specie through which benzoic acid, benzaldehyde, benzyl alcohol, benzoylglycine, m- and p-hydroxybenzoic acids, protocatechuic acid, phenyl acetic acid, cinnamic acid and p-hydroxycinnamic acid, caffeic acid, cyclohexa-2,5-dienecarboxylic acid and cyclohexanecarboxylic acid, phloroglucinol, adipic acid and pimelic acid could undergo anaerobic degradation in a nitrate-mineral salts medium. These same compounds were earlier found by Dutton and Evans (1969) to be photosynthetically metabolized under anaerobic conditions by *Rhodopseudomonas palustris*. Phenol, catechol, quinol, resorcinol, p-cresol, salicylic acid, phthalic acid, gentisic acid, phloroglucinol-carboxylic acid, phenylpropionic acid, tryptophan, cyclohexa-1,4-dienecarboxylic acid and cyclohex-3-enecarboxylic acid were not utilized by the benzoate-grown cell. Thus Williams and Evans put forth an anaerobic pathway, analogous to that suggested by Dutton and Evans (1969-Figure 1) but adapted to nitrate respiration; thus including a pathway from 2-oxocyclohexanecarboxylate (V) to either decarboxylation to cyclohexanone (VIII) or hydration to cyclohexane-1,2-diol-1-carboxylate (XIV). The latter compound or its dehydrated product could then be decarboxylated to form cyclohexanone (VII) or cyclohexane-1,2-dione (X), respectively. 2-hydroxycyclohexanone (IX) is then purported to be hydrolytically cleaved to 6-hydroxyhexanoate (XI) where dehydrogeneses could convert adipic acid semialdehyde (XII) into adipate (XIII).

Aerobic Degradation of Catechol

Dagley et al. (1960) described the aerobic degradation of catechol to be an oxidative fission of the bond between carbon atoms bearing the hydroxyl groups of an o-dihydroxyphenol, catechol, as-cis-muconic acid or its γ -carboxy derivative via pyrocatechase (Figure 3). Dagley and Stopher (1959) investigated the degradation of catechol by two strains of Gram-negative bacteria, one acclimated to m-cresol, the other to o-cresol. An enzyme called catechol 2:3-oxygenase was also found to give a different intermediate of α -hydroxymuconic semialdehyde or a derivative of this compound which is further degraded to pyruvate (Figure 4). Nishizuka et al. (1962) demonstrated that a *Pseudomonas* grown with o-cresol converted catechol into acetate and pyruvate by the reaction sequence shown in Figure 5. Catechol is first oxidized to α -hydroxymuconic semialdehyde which is then converted to γ -oxalocrotonate. Hydrolyzation gives rise to α -oxo- γ -hydroxyvalerate. This is converted to acetopyruvate which is further hydrolyzed to acetate and pyruvate. Dagley et al. (1964) proposed the variation between sequences to be a function of the *Pseudomonas* species utilized. However, further investigations by Gibson et al. (1967) showed that the overall mechanism was unaffected by NAD (nicotinamide adenine dinucleotide). The enzymetically-formed compound was identified as a 2,4-dinitrophenylhydrazone derivative, not γ -oxalocrotonate. Also, experimental results point to the formation of formic acid and not carbon dioxide.

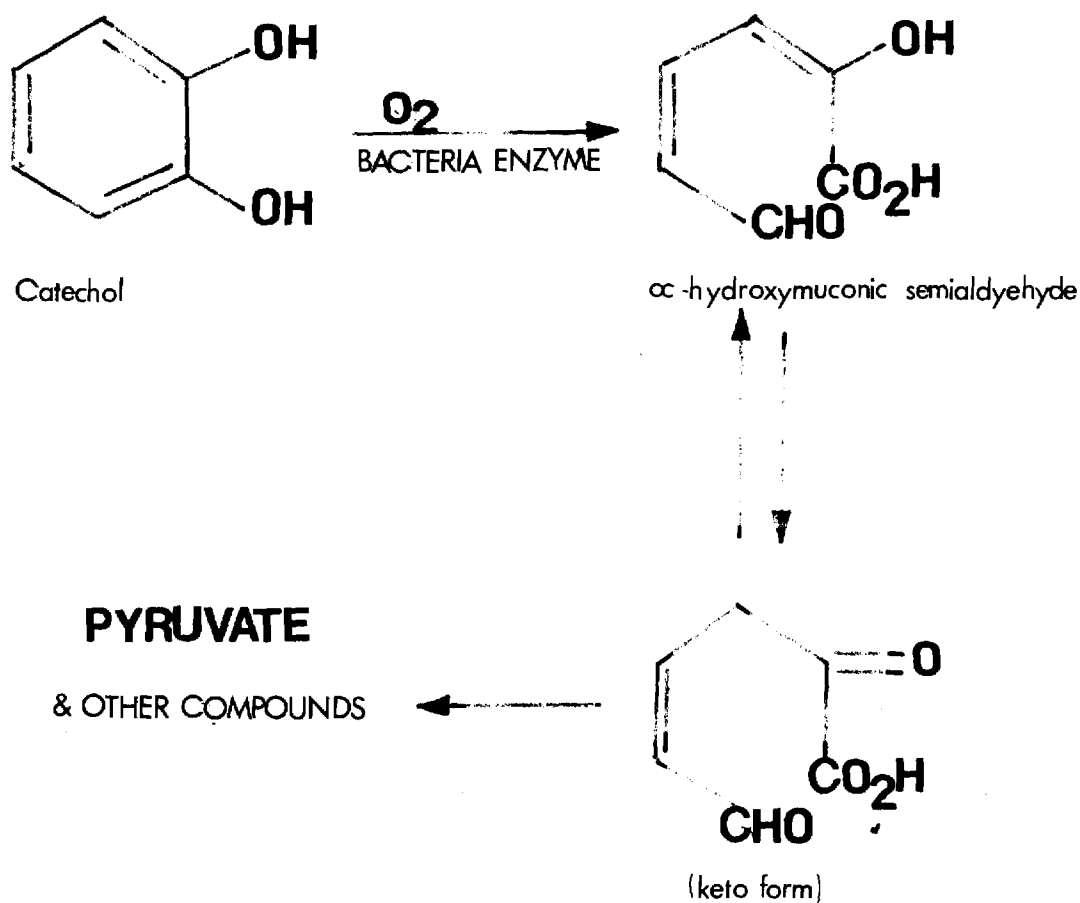
Anaerobic Filters

The anaerobic filter was first developed by McCarty (1966) for the treatment of wastewaters containing soluble organic matter. This anaerobic process is analogous to an aerobic trickling filter. The apparatus consists of a bed of solid media sealed in an oxygen-free atmosphere. The waste is



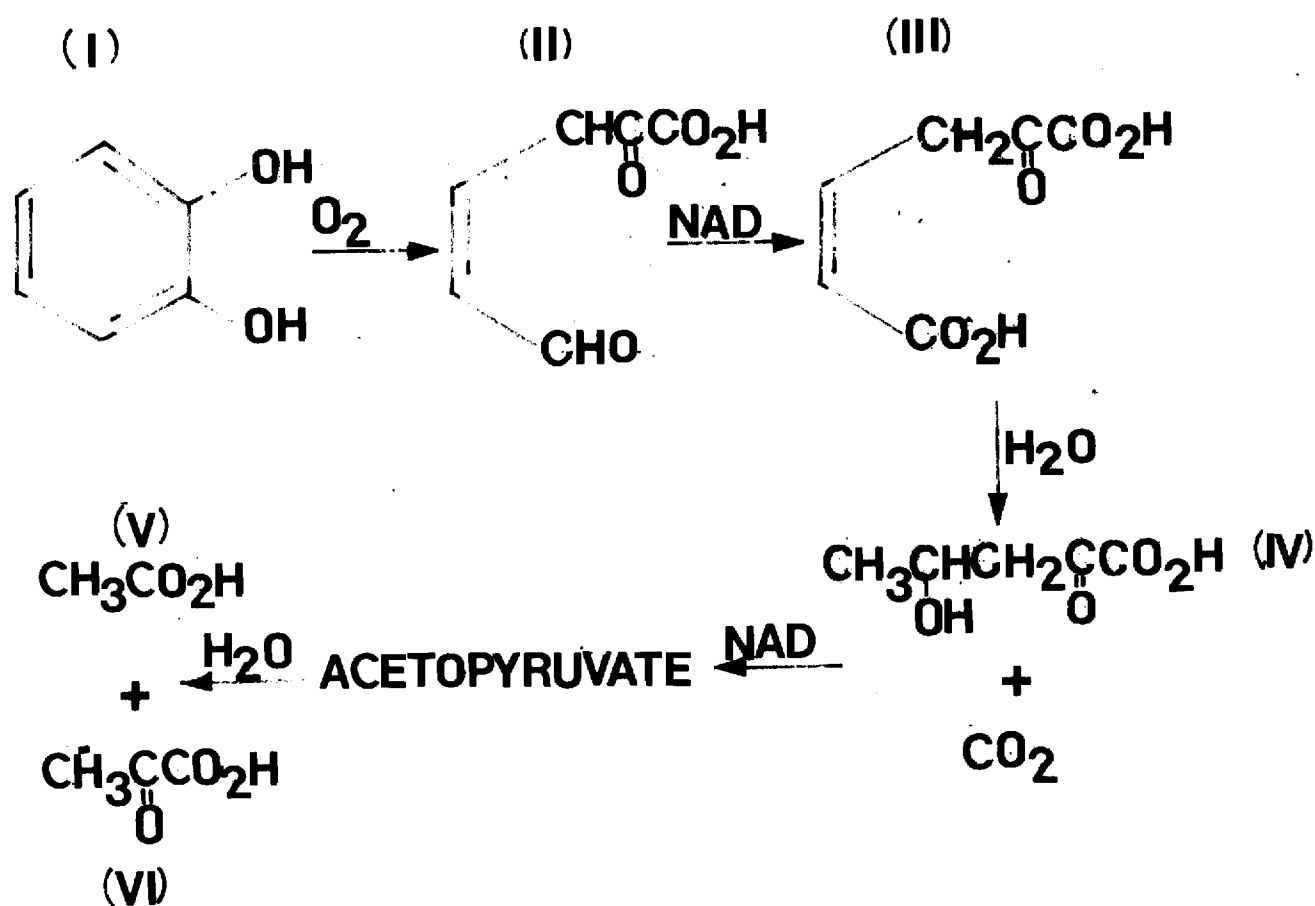
PROPOSED PATHWAY OF DISSIMILATION OF CATECHOL
(DAGLEY, EVANS & RIBBONS, 1960)

FIGURE 3



**PROPOSED PATHWAY OF CATECHOL OXIDATION
(DAGLEY AND STOPHER)¹⁵**

FIGURE 4



REACTION STEPS PROPOSED FOR CATECHOL DEGRADATION

(NISHIZUKA et al)¹⁶

FIGURE 5

applied in an upflow mode across the bottom of the anaerobic filter as to completely submerge the unit and facilitate the maintenance of an anaerobic environment. The solid media serve as attachment sites for anaerobic microorganisms and bacterial slimes that serve to stabilize the waste. These microorganisms may also accumulate in void spaces between the solid media increasing the contact of the organisms with the waste.

Young and McCarty (1967) have found the anaerobic filter to have several advantages over present biological treatment methods:

1. The ability to effectively treat soluble wastes.
2. The ability of the filter to retain biological solids eliminating the need for effluent or solids recycle.
3. The ability to accumulate biological solids also permits the treatment of dilute waste at nominal temperatures.

In addition, other advantages of the anaerobic process are (McCarty, 1964):

1. A high degree of stabilization is obtained.
2. Low nutrient requirements.
3. No oxygen requirement, and consequently low power cost.
4. The production of a useful end product, methane.

Young and McCarty (1968) utilized an anaerobic filter (6 ft long x 5.5 in. I.D.) filled with quartzite stone (1-1.5 in. in diam.) to study the performance of this process under various loading conditions. The filter was operated at a constant temperature of 25°C and was fed one of two synthetic organic substrates. One substrate consisted of a mixture of complex protein-carbohydrate and the other consisting of an equivalent COD mixture of acetic and propionic acids. Results obtained from their study are shown in Table 6. These results demonstrate the ability of the filter to sustain short duration shock loading conditions. Increases in loading rates resulted in decreased COD removal for both substrates. Moreover, effluent suspended

solids, having a volatile content in excess of 93-95 percent, increased with increased loading for the protein-carbohydrate mixture, but remained constantly low (less than 10 mg/l) for the volatile acids-waste. The investigators also found by conducting a COD-methane balance that 85 percent of the COD removed was converted to methane and carbon dioxide while only 15 percent was converted to biological solids for the protein-carbohydrate waste. The volatile acids-waste indicated almost 100 percent conversion of the COD to methane and carbon dioxide. Sampling at various heights along the column during steady state operating conditions indicate that high activity of COD removal occurred in the first 2 ft. of the filter. Thus high COD loadings which would result in high volatile acids concentration in the lower part of the column required the addition of a buffer to maintain a neutral pH.

Plummer et al. (1968) investigated the applicability of the anaerobic filter to treat a food processing carbohydrate waste with a COD of 8475 mg/l. Column heights 11 to 16 in. were filled with Raschig rings and Berl saddles and operated at a constant temperature of 35°C. pH was maintained in the range of 6.8-7.3 utilizing a buffer. Results presented in Table 7 showed increased organic loading, 101 to 638 lb. COD/1000 cu. ft./day, accompanied with decreasing hydraulic detention time (83 to 3 hrs) effected a decrease from 87 to 41 percent in the COD removal efficiency and a decrease of 95.2 to 28.3 percent in the removal efficiency of TOC. Gas content stabilized at approximately a high of 57 percent methane and a low of 32 percent methane for the respective loadings. High effluent suspended solids demonstrated the inability of a short filter to retain solids.

Lovan and Forsee (1971) operated an anaerobic filter (6 ft long x 6 in I.D.) filled with crushed limestone (1-1.5 in.) at 35°C to treat a brewery press liquor waste. The waste is characterized by a high concentration of dissolved organics and a low concentration of suspended solids with an

Table 6
Anaerobic Filter Treatment of Protein-Carbohydrate/Volatile Acids Wastewaters
(Young and McCarty, 1967)

Influent COD (mg/l)	Theoretical Detention Time (hr)	Organic Loading (lb COD/day/1000 ft ³)	Effluent Quality			
			Protein Suspended Solids (mg/l)	Carbohydrate/Volatile Acids Soluble COD (mg/l)	Total COD (mg/l)	Percent Removal
1500	36	26.5	9/3	100/20	112/24	92.1/98.4
1500	18	53.0	6/3	110/135	122/139	91.5/90.5
1500	9	106.0	5/3	300/310	312/314	79.3/79.0
1500	4.5	212.0	250/4	600/470	950/476	36.7/68.4
3000	72	26.5	24/4	170/36	204/42	93.4/98.6
3000	36	53.0	48/4	280/230	347/240	88.4/92.0
3000	9	212.0	178/-	845/-	1105/-	63.0/-

Table 7
Anaerobic Filter Treatment of Food Processing Carbohydrate Wastes
(Plummer et al., 1968)

<u>Hydraulic Detention Time (hr)</u>	<u>Organic Loading (lb COD/day/1000 ft³)</u>	<u>Suspended Solids (mg/l)</u>	<u>Effluent Quality</u>				<u>Alkalinity (mg/l as CaCO₃)</u>	<u>pH</u>
			<u>COD (mg/l)</u>	<u>Percent COD Removal</u>	<u>TOC (mg/l)</u>	<u>Percent TOC Removal</u>		
83	101	455	546	93.6	115	95.2	3760	7.1
60	237	954	2405	71.6	709	70.5	2790	7.1
21	438	1554	4850	42.8	1678	30.1	2750	6.8
13	638	1855	5000	41.0	1720	28.3	2845	6.7
Influent waste		1508	8475		2400		3330	7.3

influent COD ranging in strength from 6000-24000 mg/l. A COD removal efficiency of approximately 90 percent was obtained in the lower 6 in. of the column at an organic loading of 100 lbs. COD/1000 cu.ft./day and a hydraulic detention time of a few days. This is similar to results obtained by Plummer et al. (1968). The gas content for the filter was approximately 65 percent methane and 35 percent carbon dioxide.

Studies were conducted by Taylor (1971) on a full scale model (20 ft. high x 30 ft. in diameter) of an anaerobic filter in Spokane, Washington, utilizing a rock packing media (1-2 in. in the top half, 2-3 in. in the bottom half) in the treatment of a starch plant waste stream. The results of the study served to emphasize the economic and operational feasibility of such a process. The wheat starch waste had a COD level of 5930-13000 mg/l and suspended solids level of 370-8360 mg/l. For a COD loading of 273 lbs. COD/1000 cu. ft./day and a detention time of 22 hr., a COD removal efficiency of 65 percent and an effluent suspended solids of 200-3360 mg/l were obtained.

El-Shafie and Bloodgood (1973) investigated the performance of six anaerobic filters, each 15 in. long and 5.5 in. in diameter with a bed of 1-1.5 in. gravel, placed in series and operated at a constant temperature of $30 \pm 1^{\circ}\text{C}$. The waste utilized was "Metracal" which has a COD of 11,800 mg/l. It was observed that the pH varied from 6.52 in the first filter effluent characterized by a high volatile acid concentration and low alkalinity to a pH of 7.50 in the last filter effluent characterized by low volatile acid concentrations and high alkalinity. A maximum COD removal efficiency of 70 percent was obtained for the entire unit at an organic loading of 2560 lbs. COD/1000 cu. ft./day. However, COD concentrations of the filtered effluent were observed to increase with time giving rise to a possible pH toxicity.

Jennett and Dennis (1975) studied the treatability of a pharmaceutical waste using an anaerobic filter (3 ft. (0.915 m) high x 5.5 in. (0.14 m) in diameter) filled with quartzitic gravel (1-1.5 in. in diameter) and operated at 37°C. The waste was characterized by a variable COD of 1250-16000 mg/l, 95 percent of the COD being attributable to methanol. For COD loadings of 14-220 lbs. COD/1000 cu.ft./day, COD removal efficiencies of 94-98 percent were obtained with corresponding effluent suspended solids concentrations of 10-60 mg/l, respectively. Sacks et al. (1978) found similar results when dealing with a synthesized pharmaceutical waste using an anaerobic column 48 in. high and 5.5 in. in diameter. At an organic loading of 34.9 lbs. COD/1000 cu.ft./day (0.56 kg COD/cu.m/day) and using a waste strength of 2000 mg/l, COD removal efficiencies of 70-80 percent were obtained. Effluent suspended solids were usually below 50 mg/l.

Another industrial application for the anaerobic filter has been in the treatment of a vegetable tanning waste. The waste treated was characterized by high concentrations of tannin which consist of pyrogallol and catechol groups. Arora et al. (1975) operated two filters, 1.85 m in depth and 140 mm in diameter at a temperature of 30°C \pm 5°C and a pH range of 7.0-8.2. The filters were fed individually with an untreated waste and a waste supplemented with phosphate to maintain a N:P ratio of 40:1. The results obtained found no profound difference in COD behavior between the supplemented and unsupplemented waste. COD reduction of 20-80 percent was obtained for organic loadings of 3.264 kg/m³/day-1.344 kg/m³/day, respectively. A large percentage of the effluent COD was attributable to tannin. Therefore at high loadings of tannin, the system was inhibited whereas at the lower loading rates these compounds were well degraded.

Mueller and Mancini (1975) experimented with two 6½ ft. long x 5" I.D. columns filled with 5/8 in. polypropylene rings using a synthetic protein-carbohydrate organic feed. A magnetic stirring bar was housed at the bottom of the columns to provide for even influent distribution. The investigators obtained COD removals of 90 percent and 50 percent utilizing detention times of 24 to 3 hr. at loadings of 200 to 1700 lbs. COD/1000 cu. ft./day, respectively. In modeling the anaerobic filter, Mueller and Mancini observed that filter performance can be adequately approximated using a combination of first order kinetics and a measured volatile solids concentration profile. Comparing their results with those obtained from other studies on the anaerobic filter, the investigators were able to obtain values for the rate constant ranging from 0.00042 to 0.00045 (mg/l-day)⁻¹ for rock media at 25°C while higher values of 0.0005 to 0.0007 (mg/l-day)⁻¹ applied to data obtained from plastic media filled filters operated at 35°C. A rate constant of 0.001 (mg/l-day)⁻¹ fitted the volatile acid data for both filters except for the highly loaded plastic media filter where methanogenic activity may have been inhibited.

Chian and DeWalle (1977) investigated the use of a completely mixed reactor 246 cm in length and 20.2 cm I.D. to treat a high strength acidic wastewater. The waste, leachate from solid waste landfills, was characterized by a COD of 54,000 mg/l and a pH of 5.4. The leachate contains fatty acids (49 percent of the COD), 1610 mg/l carbohydrates, 605 mg/l tannins, 1270 mg/l proteins, 2200 mg/l Fe, 104 mg/l Zn, 18 mg/l Cr, 13 mg/l N and 0.5 mg/l Cu. A plastic "Surpac" slab having a specific density of 1.45 g/cm³ was utilized as the filter medium. The anaerobic filter was operated in an upflow mode using a diluted waste of 1:2 with an adjusted influent pH of 7.

A recirculation ratio of 1:20 was used to further dilute the waste and to improve the buffering capacity of the aqueous phase. The system was overloaded on three separate occasions by reduction of the detention time from 42 days to 7, 4.25, and 3 days. These shock loading conditions resulted in a slight pH drop and higher effluent organic content due to the resuspension of the solids. Restoration of the detention time from 3 to 42 days resulted in effluent values of COD and suspended solids slightly higher than those obtained prior to the shockloadings. Heavy metal toxicity was also evident as demonstrated by a gradual reduction in methane production, a lowering in pH, an increase in effluent concentrations of fatty acids, carbohydrate and aromatic hydroxyl groups, and the corresponding increase in effluent COD. The addition of sulfide to alleviate the toxicity resulted in a decreased ORP and reduced heavy metal concentrations. The investigators concluded from their studies that high organic matter removal occurred at hydraulic detention times exceeding 7 days where 93 percent of the COD removed could be accounted for as gas produce. Chian and DeWalle also observed that the effluent solids concentration was dependent on the hydraulic detention time and filter porosity. The latter parameter, as measured in previous studies, showed that a low void ratio resulted in low suspended solids concentration. For example: suspended solids of 10 mg/l at a void ratio of 0.42 (Young and McCarty, 1968), 34 mg/l at a void ratio of 0.47 (Jennett and Dennis, 1975), 40 mg/l at a void ratio of 0.46 (Forsee and Reid, 1973), 450 mg/l at a void ratio of 0.85 (Mueller and Mancini, 1975), 1200 mg/l at a void ratio of 0.68 (Plummer et al., 1968) and 190 mg/l at a void ratio of 0.94 (Chian and DeWalle, 1977). The latter values vary due to shorter detention times (13-83 hr.) and longer detention times (3-42 days), respectively.

Other applications of the anaerobic filter have been in the denitrification of agricultural subsurface drainage. Tamblyn and Sword (1969) and Pafford et al. (1971) studied the disposal of saline waters in the San Joaquin Valley in California. Experimental units were constructed of polyvinylchloride in 18 in. and 36 in. diameters and 6.5 ft. high. Pafford et al. found the most feasible medium in terms of nitrogen removal was 1.0 in. diameter rounded aggregate. Use of this media resulted in reducing nitrite-nitrogen levels from 30 mg/l to 2 mg/l at water temperatures of 12-16°C with a 6 hr. detention time and 15 mg/l to 2 mg/l at water temperatures of 20-24°C at a 1 hr. detention time. Tamblyn and Sword using filters containing 0.164 and 0.067 in. diameter activated carbon, 0.012 in. diameter washed sand or 3/8 in. diameter aggregates found that 80 percent of the nitrogen applied was removed regardless of media. Experimenting further with rounded aggregates (3/8 and 1 in. diameter), angular bituminous coal (5/16 and 1 in. diameter), volcanic cinders (5/16, 5/8 and 1 in. diameter), 0.164 in. diameter activated carbon and 0.012 in. diameter washed sand as filter medias, Tamblyn and Sword found that medium surface texture and sorptive quality did not appreciably affect removal efficiencies. There was also no apparent difference between the removal efficiencies of filters containing similar media of different sizes. However with long term operations at hydraulic detention times of 0.5-2 hrs., variations in nitrogen removal efficiencies occurred due to short circuiting for sand. Higher head losses and lower nitrogen removal also occurred for filters with media size less than 1 inch.

Norrman and Frostell (1977) combined two processes, the contact process with the anaerobic filter to treat dilute wastewaters in order to achieve an efficient separation of solids at a logical hydraulic detention time. The 20 l hydrolysis reactor, sludge separator and 20 l anaerobic filter filled

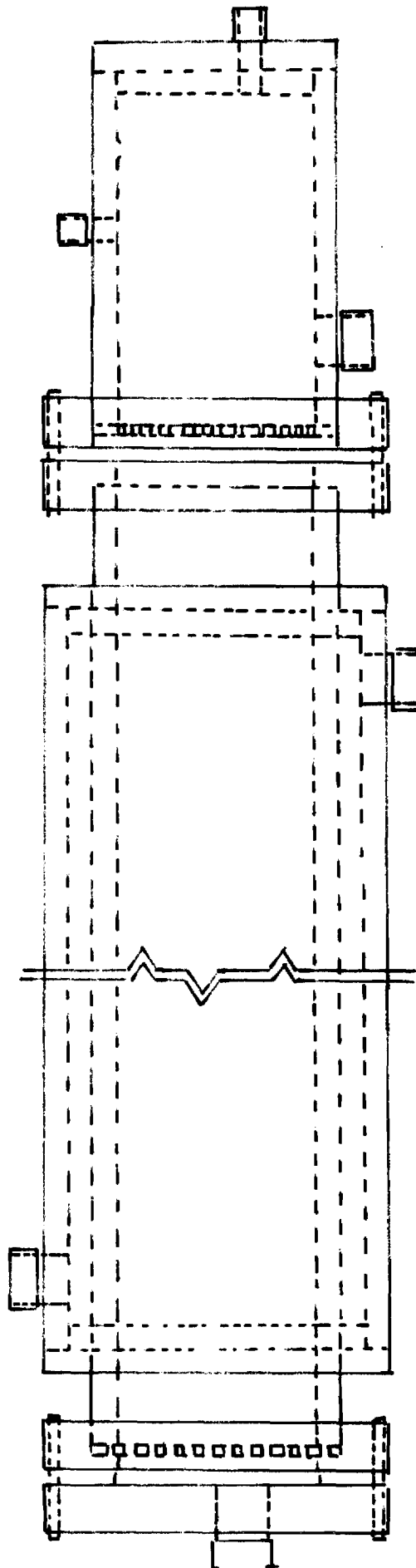
with 1-2 cm crushed stone-media were all placed in series. The FRONO-reactor operated at 33°C and hydraulic detention times of 13.6 to 4.1 days. The influent COD of 3800-9500 mg/l was reduced 93-99 percent, respectively. Much more work is still needed, however, in order to better understand the relative merits of this treatment configuration.

MATERIALS AND METHODS

Experimental Apparatus

Two identical experimental reactors were used in this study. Each experimental reactor consisted of four jacketed columns and three clarifiers connected in series with one clarifier located after each of the first three columns. Figure 6 represents a schematic of one jacketed column. Each column was constructed of 0.64 cm (0.25 inch) wall plexiglass tubes having a 5.08 cm (2 inch) internal diameter and 60.96 cm (24 inch) in length. A 0.32 cm (0.125 inch) thick and 5.715 cm (2.25 inch) in diameter perforated plate was placed at the top and bottom of each column in order to retain all particles larger than 0.32 cm (0.125 inch) within the column. The lower plate was glued to the bottom of the column and held in place between the column and a 1.27 cm (0.5 inch) base plate. Two fittings were placed in the base plate in order to allow for entry into the column of the feed solution and the recirculated flow (see Figure 6). The upper perforated plate is situated between the top of a column and a 10.16 cm (4 inch) long capped cylinder constructed of the same plexiglass tube that was used to build the main body of the column. Three fittings were placed in the top section of each column. These fittings were for (a) effluent withdrawal situated 3.18 cm (1.25 inch) from the top, (b) recycle flow withdrawal situated 5.72 cm (2.25 inch) from the top and (c) gaseous products exit situated on the very top of the 10.16 cm extension to the column.

A thermal water jacket was constructed around the main body of each column using 0.64 cm (0.25 inch) wall cylindrical plexiglass tube 57.79 cm (22.75 inch) long and 7.62 cm (3 inch) in internal diameter. Each water jacket had two fittings situated 1.27 cm (0.5 inch) from each end of the

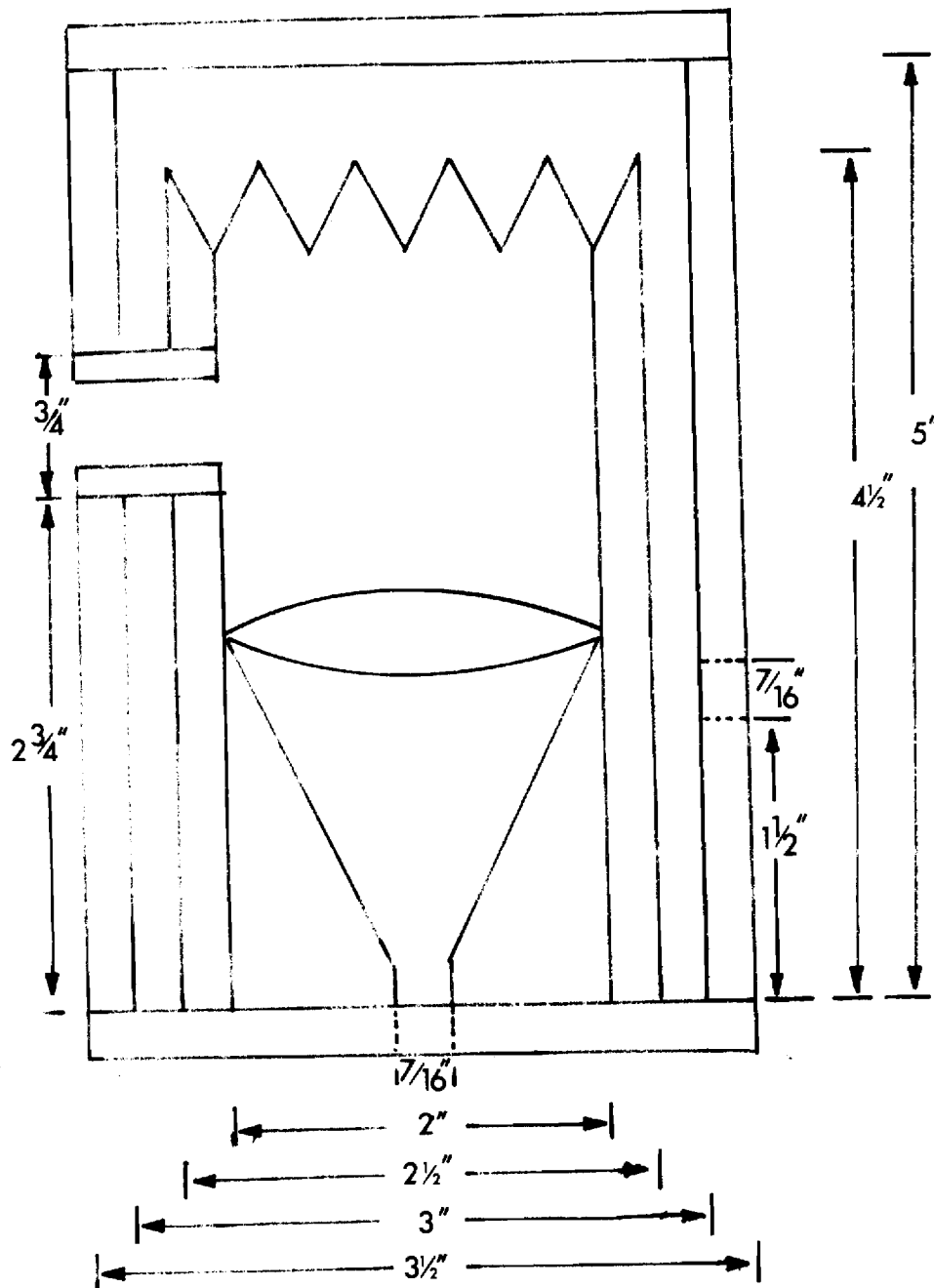


**COLUMN
SCHEMATIC
FIGURE 6**

jacket. The water jackets of all eight columns were connected in series using Imperial Eastman Poly-flo tubing 66-p-3/8 to the inlet of the recirculating pump of a constant temperature bath (American Instrument Model No. 4-8600) while the flow from the jacket of the last column was returned to the same temperature bath. Water was recirculated at a high flow rate through the water jackets in order to maintain a constant and uniform temperature of $35 \pm 0.5^{\circ}\text{C}$ throughout the experimental apparatus.

The aqueous contents of every reactor were continuously recirculated around that reactor using a multiple head tubing pump (Cole-Parmer Model 7567 with Cole-Parmer Masterflex Pumpheads #7018-20). A combination of 1.27 cm (0.5 inch) outer diameter Tygon Flexible Plastic tubing and Cole-Parmer 6408-09 Tygon tubing having an outer diameter of 1.11 cm (0.44 inch) were used for recirculation. The feed substrate, the effluent from every column and the final effluent were all conducted through 0.66 cm (0.25 inch) outer diameter Imperial-Eastman Poly-flo tubing 44-p-1/4. Similar tubing was used to connect each gas release fitting to the corresponding gas collection system. Each gas collection system consisted of a 1 l buret, 1 l balancing bottle, and one gas release and sampling T-connection and 1 l of acid solution containing methyl orange indicator. The function of the acidic solution was to minimize the dissolution of the carbon dioxide present in the gas buret.

An inline check valve was placed between each column and its corresponding clarifier in order to prevent any accidental backflow through the system. The clarifiers were employed in order to provide a means for the removal of excess biomass from the columns and to provide a separation between the gaseous phases of the different columns. These clarifiers (see Figure 7) were constructed of 0.66 cm (0.25 inch) wall plexiglass tubes having a 7.62 cm (3 inch)



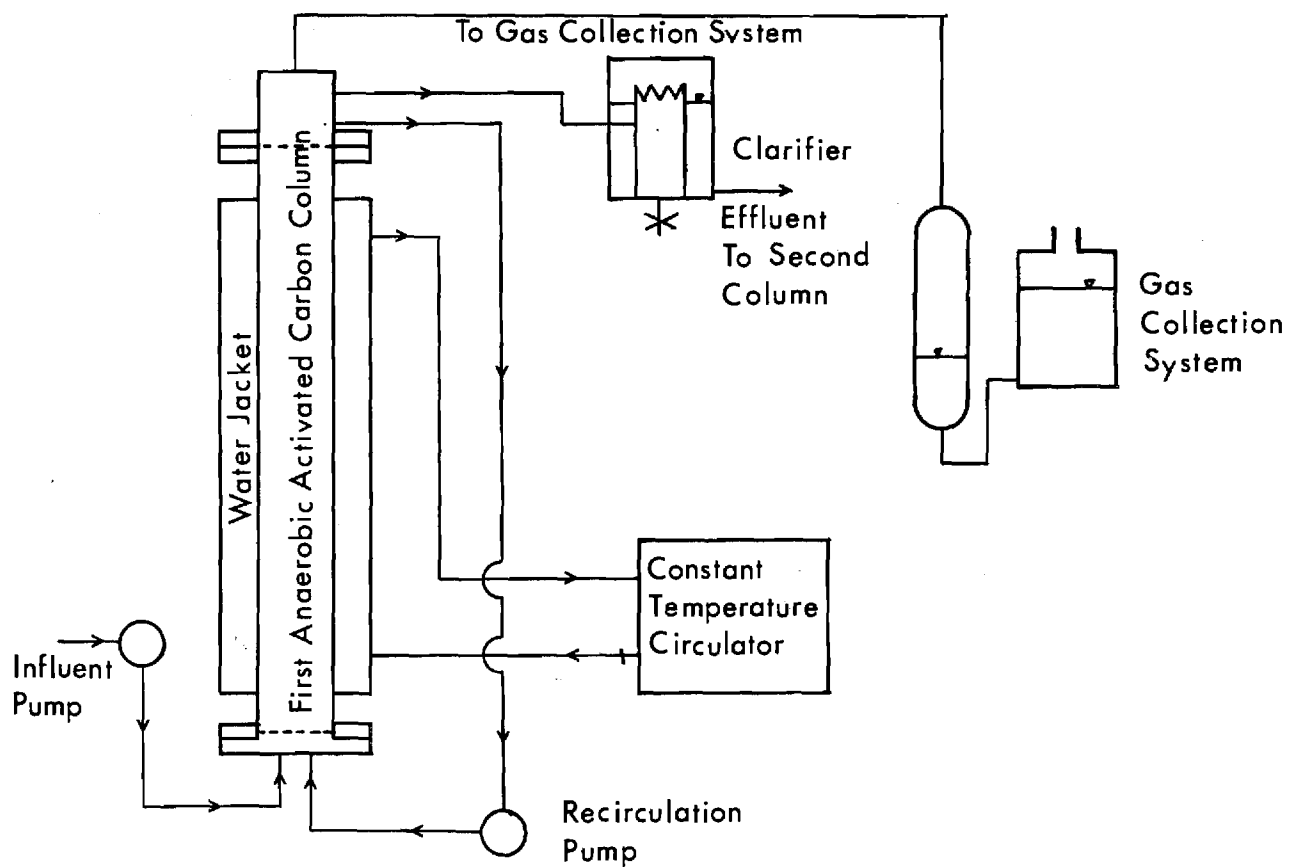
SCHEMATIC OF CLARIFIER
FIGURE 7

internal diameter and 12.7 cm (5 inch) long. The internal weir structure of the clarifier was constructed of a 0.66 cm (0.25 inch) wall plexiglass tube 5.08 cm (2 inch) in internal diameter and 11.43 cm (4.5 inch) long. The weir was provided with a V-shaped notch and an inner cone was situated within the inner tube structure to provide for more efficient removal of settled biomass through a 1.11 cm (7/16 inch) sampling port located at the bottom of the clarifier. A schematic of the first anaerobic activated carbon filter and the associated clarifier and gas collection system is shown in Figure 8.

Granular Activated Carbon Contact Medium

Granular activated carbon was used as a packing medium for the anaerobic filters utilized in this study. The specific commercial activated carbon employed in this research was bituminous base Filtrasorb 400 (Calgon Corporation, Pittsburg, PA). This activated carbon was first sieved into a number of particle size fractions (see Table 8). The individual fractions were then washed with distilled water to eliminate fines and subsequently dried at 105-110°C for forty-eight hours. The specific characteristics of the carbon as given in the manufacturer's bulletin (Calgon Corporation, 1976) are reproduced in Table 9, while the pore volume-pore radius distribution is presented in Figure 9.

Each anaerobic filter column was charged with 446.6 grams of activated carbon. Only the granular size fractions of the sieved, washed and dried Filtrasorb 400 falling within the 10 x 20 U.S. Standard Mesh size was used in this study. The selection of this particular size range was made primarily because this size range represents sufficiently large particles which will minimize clogging problems due to the carbon retaining perforated plates at the end of the reactors. In addition, this size range constituted the major fraction by weight,



SCHEMATIC OF SINGLE ANAEROBIC FILTER COLUMN

FIGURE 8

Table 8. Sieve Analysis Data on Filtrasorb 400 Activated Carbon

Sieve # U.S.S.M.	Sieve Size (mm)	Weight Retained (g)	Cumulative Weight Retained (g)	Percent Weight Retained
6	3.36	0	0	0
8	2.38	0	0	0
10	2.00	0.11	0.11	0.022
16	1.18	208.03	208.14	41.94
18	1.00	99.53	307.67	62.00
20	0.85	57.20	364.87	73.52
30	0.59	98.66	463.53	93.41
40	0.42	24.10	487.63	98.26
50	0.297	6.51	494.14	99.57
80	0.179	1.53	495.67	99.88
100	0.149	0.33	496.00	99.95
170	0.088	0.18	496.18	99.98
Pan	<0.088	0.06	496.24	100.00

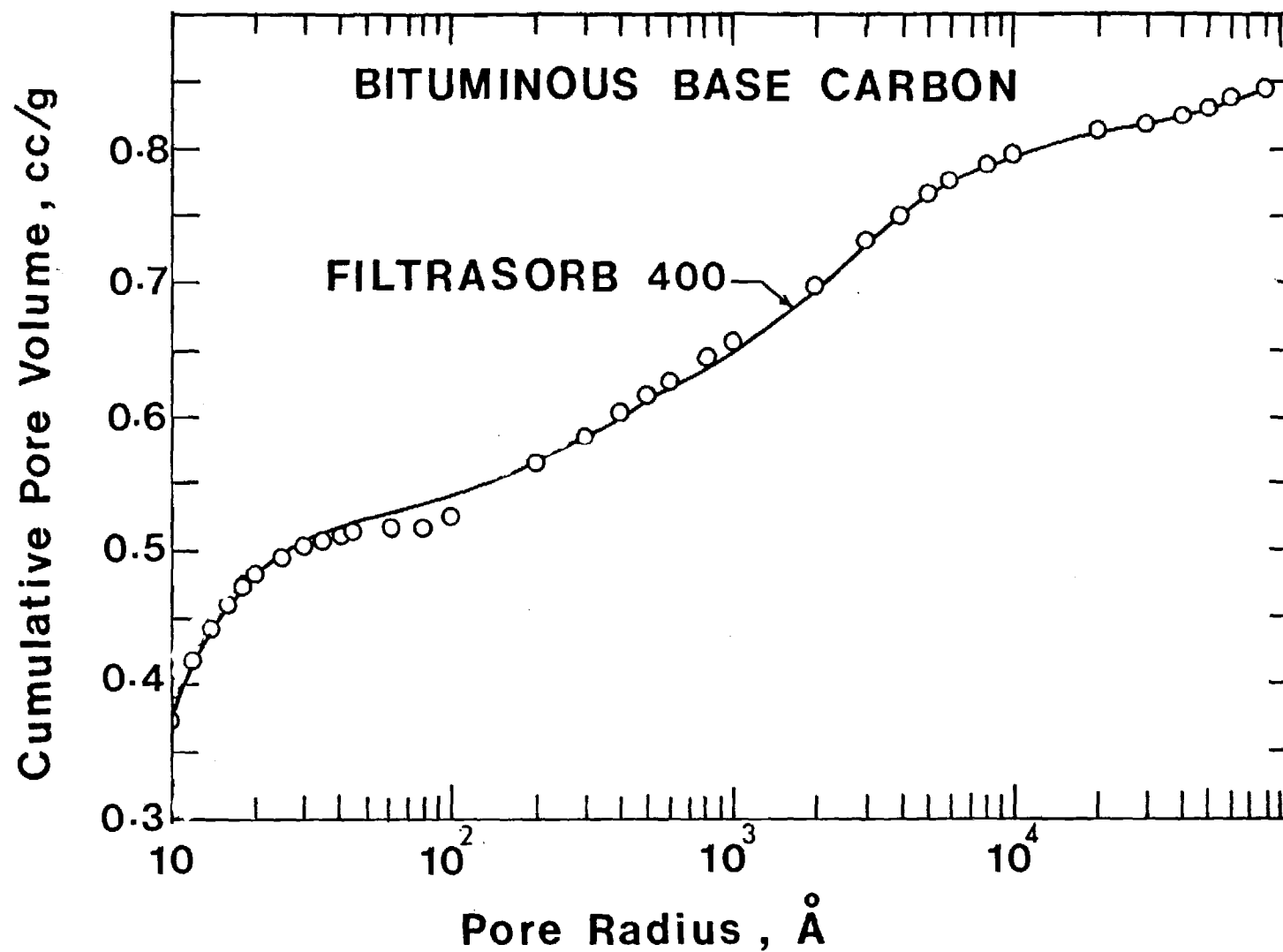
Table 9. Physical Properties of Filtrasorb 400
(Calgon Corporation, 1976)

Total Surface Area (N ₂ BET Method) m ² /g	1050 - 1200
Bulk Density, lb/ft ³	25
Particle Density Wetted in Water, g/cc	1.3 - 1.4
Pure Volume, cc/g	0.94
Effective Size, mm	0.55 - 0.65
Uniformity Coefficient	1.6 - 2.1

74 percent, of the commercial carbon Filtrasorb 400. The specific make up of the carbon employed was: (a) 16 percent by weight 18 x 20 U.S. Mesh, (b) 27 percent by weight 16 x 18 U.S. Mesh, and (c) 57 percent by weight 10 x 16 U.S. Mesh.

Synthetic Feed Substrate

Synthetic catechol and Cresol bearing substrates were used in this investigation in order to determine the fate of these phenolic compounds in the anaerobic activated carbon filter. These substrates were prepared daily in



PORE SIZE DISTRIBUTION

FIGURE 9

4 & glass reservoirs and were introduced into the first column of every set of reactors using positive displacement FMI pumps, Model RPG - 20 (Fluid Metering Incorporated, Oyster Bay, NY). Each pump was rated at a maximum flow rate of 5.4 ml/min and a maximum operating pressure of 50 psi. The synthetic substrates were fed into the respective systems at a flow rate of 2 ml/min. At this flow rate, an empty bed contact time of 11.62 hours was provided per reactor resulting in a total empty bed contact time of 46.67 hours for the entire system.

Trace Salt Solution. A concentrated stock solution of various trace salts and the complexing agent, sodium citrate, was prepared in 2 liter batches in distilled water according to the formulation given in Table 10.

Salt Solution. Each liter of the stock salt solution was prepared by adding the components indicated in Table 11 to distilled water.

The vitamin extract was prepared by the addition of 10 g of Alacer A to Zinc Multimineral^R to a mixture of 250 ml of ethanol and 250 ml of distilled water. This solution was heated to a temperature of 50°C, stirred for 24 hours and then allowed to settle. The decanted supernatant was utilized as the extract.

Table 10. Composition of Trace Salt Solution

<u>Compound</u>	<u>Quantity (grams)</u>
FeCl ₃	38.88
MnCl ₂ • 4H ₂ O	9.48
ZnCl ₂	6.54
CaCl ₂ • 2H ₂ O	4.10
CoCl ₂ • 6H ₂ O	5.71
Na ₂ B ₄ O ₇ • 10H ₂ O	2.29
Na ₃ Citrate	353.00
(NH ₄) ₆ Mo ₇ O ₂₄ • 4H ₂ O	4.15

Dilute to a total volume of 2 liters

Table 11. Composition of Salt Solution

<u>Compound</u>	<u>Quantity</u>
Trace Salt Solution	33.3 ml
KH_2PO_4	13.61 grams
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	8.28 grams
$(\text{NH}_4)_2\text{SO}_4$	5.28 grams
NH_4Cl	25.00 grams
CaCl_2	4.44 grams
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	8.13 grams
Vitamin Mixture	35.00 ml
Cysteine Hydrochloride Solution	5.00 ml

Dilute to a total volume of 1 liter

The cysteine hydrochloride solution was prepared by dissolving 10 g of sodium thiosulfate and 0.1 g of cysteine hydrochloride in distilled water to make 1 l of solution.

Phosphate Buffer. A three molar phosphate buffer solution was prepared by adding 261.29 g of K_2HPO_4 and 179.96 g of NaH_2PO_4 or 212.96 g of Na_2HPO_4 and 202.60 g of KH_2PO_4 to distilled water in order to make up one liter of buffer solution.

Catechol Substrates. The catechol fed anaerobic activated carbon filter was operated in three phases. During the first phase a feed catechol concentration of 200 mg/l was used while in the second and third phases the catechol concentration in the feed was increased to 400 and 1000 mg/l, respectively.

The catechol substrate was prepared daily in 4 l batches. Each batch was prepared by adding specific volumes of the salt and buffer solutions along with

a weighed quantity of catechol to distilled water resulting in a final volume of 4 liters of substrate. Prior to introduction into the system, the pH of the feed substrate was adjusted using a 10 N solution of sodium hydroxide and the reservoir and contents were purged with nitrogen gas in order to displace the dissolved oxygen. The substrate reservoir was then placed in a refrigerator from which it was pumped into the treatment system. The composition of the feed substrate for each phase is given in Table 12.

Table 12. Composition of Synthetic Catechol Bearing Substrate*

Compound	Phase 1	Phase 2	Phase 3
	Concentration 200 mg/l Catechol	Concentration 400 mg/l Catechol	Concentration 1000 mg/l Catechol
1. FeCl ₃	2.27	4.53	8.09
2. MnCl ₂ • 4H ₂ O	0.55	1.10	1.97
3. ZnCl ₂	0.38	0.76	1.36
4. CaCl ₂ • 2H ₂ O	0.24	0.48	0.85
5. CoCl ₂ • 6H ₂ O	0.33	0.67	1.19
6. Na ₂ B ₄ O ₇ • 10H ₂ O	0.13	0.27	0.48
7. Na ₃ Citrate	20.57	41.14	73.47
8. (NH ₄) ₆ Mo ₇ O ₂₄ • 4H ₂ O	0.24	0.48	0.86
9. KH ₂ PO ₄	47.64	95.27	170.13
10. NaH ₂ PO ₄ • H ₂ O	28.98	57.96	103.50
11. (NH ₄) ₂ SO ₄	18.48	36.96	66.00
12. NH ₄ Cl	87.50	175.00	312.50
13. CaCl ₂	15.54	31.08	55.50
14. MgCl ₂ • 6H ₂ O	28.46	56.91	101.63
15. Vitamin Mixture Ethanol Extract	0.123	0.245	0.438
16. Cysteine Hydro- chlorid Solution	0.0175	0.035	0.063
17. K ₂ HPO ₄	5225.80	5225.80	5225.80
18. NaH ₂ PO ₄	3599.20	3599.20	3599.20
19. Catechol	200.00	400.00	1000.00

* All concentrations in mg/l except 15 and 16 in ml/l

O-Cresol Substrate. The o-cresol fed anaerobic activated carbon filter was operated using a feed o-cresol concentration of 256 mg/l.

The o-cresol substrate was prepared daily in 4 l batches. Each batch was prepared by adding specific volumes of the salt and buffer solutions along with 1 ml of o-cresol. Distilled water was used to bring the final feed volume to 4 l. Prior to use, the pH of the feed substrate was adjusted using a 10 N solution of sodium hydroxide and the reservoir and contents were purged with nitrogen gas. The reservoir was then placed in a refrigerator from which the substrate was pumped to the first column of the o-cresol fed anaerobic reactor system. The composition of the feed substrate for this experiment is given in Table 13.

Table 13. Composition of Synthetic O-Cresol Bearing Substrate*

<u>Compound</u>	<u>Concentration</u> <u>256 mg/l O-Cresol</u>
1. FeCl ₃	5.50
2. MnCl ₂ · 4H ₂ O	1.34
3. ZnCl ₂	0.93
4. CaCl ₂ · 2H ₂ O	0.58
5. CoCl ₂ · 6H ₂ O	0.81
6. Na ₂ B ₄ O ₇ · 10H ₂ O	0.32
7. Na ₃ Citrate	49.96
8. (NH ₃) ₆ Mo ₇ O ₂₄ · 4H ₂ O	0.59
9. KH ₂ PO ₄	57.84
10. NaH ₂ PO ₄ · H ₂ O	35.19
11. (NH ₄) ₂ SO ₄	22.44
12. NH ₄ Cl	106.25
13. CaCl ₂	18.87
14. MgCl ₂ · 6H ₂ O	34.55
15. Vitamin Mixture	
Ethanol Extract	0.149
16. Cysteine Hydrochloride Solution	0.021
17. K ₂ HPO ₄	2220.97
18. NaH ₂ PO ₄	1429.66
19. O-Cresol	256.00
20. Glucose	0.00

* All concentrations in mg/l except 15 and 16 are in ml/l

Reactor Operation

The schematic diagram of the first column and clarifier of a reactor

system is illustrated in Figure 8. The substrate was fed to the bottom of the first column from the substrate reservoir using a variable speed positive displacement FMI pump, Model RPG-20 (Fluid Metering Incorporated, Oyster Bay, NY). Both pump and reservoir were placed in a refrigerator maintained at 6°C. The substrate was forced upflow through the column. Continuous recirculation of the contents of the first column back to the column inlet was exercised while the effluent was transmitted onwards to the clarifier through a check valve. Any gas produced was collected and measured in the gas buret. The effluent from the first clarifier provided the feed to the second column clarifier configuration and the same was repeated in the third and fourth column clarifier arrangements.

Microbial growth in the feed lines and feed reservoirs was minimized through the daily cleaning of the lines and feed reservoirs.

Reactor Startup

All the anaerobic filters were initially seeded with the supernatant obtained from an anaerobic sludge digester operated by the City of Atlanta at The Clayton Wastewater Treatment Plant. All columns were batch fed with the appropriate catechol or o-cresol bearing substrates for a period of 10 days. During this period recirculation of the aqueous contents of each individual filter was exercised in a downflow manner in order to allow the microorganisms to spread throughout the activated carbon medium. After this initial period, the synthetic substrates were continuously fed into the two reactor systems at a flow rate of 5 ml/min and a feed phenolic concentration of 100 mg/l, which after 10 days was increase to 200 mg/l.

No microbial activity was observed from either of the two experimental units for a continuous operating period of 70 days. This lack of gas production

may be attributed to the combined effect of adsorption of the phenolic compounds onto the carbon surface and a consequent starvation of the organisms, and to the washout of the anaerobic culture at the initial operating conditions.

This situation was remedied on the seventieth day of continuous operation when the two reactor systems were: (a) reseeded with an acetate acclimated methanogenic culture, (b) the feed flow rate was reduced for the remaining period of study down to 2 ml/min and the catechol and o-cresol feed concentrations were maintained at 200 and 256 mg/l, respectively. The choice of an o-cresol feed concentration of 256 mg/l was made for ease of measurement of this substrate. The recirculation flow was set at 50 ml/min for all columns. As will be discussed in the subsequent chapters, the o-cresol fed reactor was reseeded a number of times and after each reseed, the recirculation flow was reversed to a downflow manner for a period of one week.

Sampling Procedure and Data Collection

Two T-connections were installed in the recirculation line of each anaerobic filter. Samples were withdrawn from the feed reservoir and the recirculation line of every column and analyzed twice a week. These analyses included:

- (a) pH
- (b) Total Inorganic Carbon (TIC)
- (c) Total Organic Carbon (TOC)
- (d) Chemical Oxygen Demand (COD)
- (e) Catechol or O-Cresol Concentration
- (f) Volatile Fatty Acids

In addition, the gaseous products from each individual column were measured daily, corrected for moisture content, and converted to standard temperature and pressure using the following equation:

$$V_{D,STP} = V \left(\frac{273.16}{273.16 + T} \right) \left(1 - \frac{V_P}{760} \right) \quad (3)$$

Where:

- T = the room temperature taken in the vicinity of the gas buret, °C;
- V = the measured volume of gas produced at 1 atmosphere, ml;
- V_P = water vapor pressure at temperature T, mm of mercury; and
- V_{D,STP} = dry gas produced at standard temperature and pressure, ml.

The gas produced was analyzed twice a week for methane, carbon dioxide, hydrogen, nitrogen, and oxygen.

Once study state was reached, additional analyses were conducted for a period of three weeks. These analyses included:

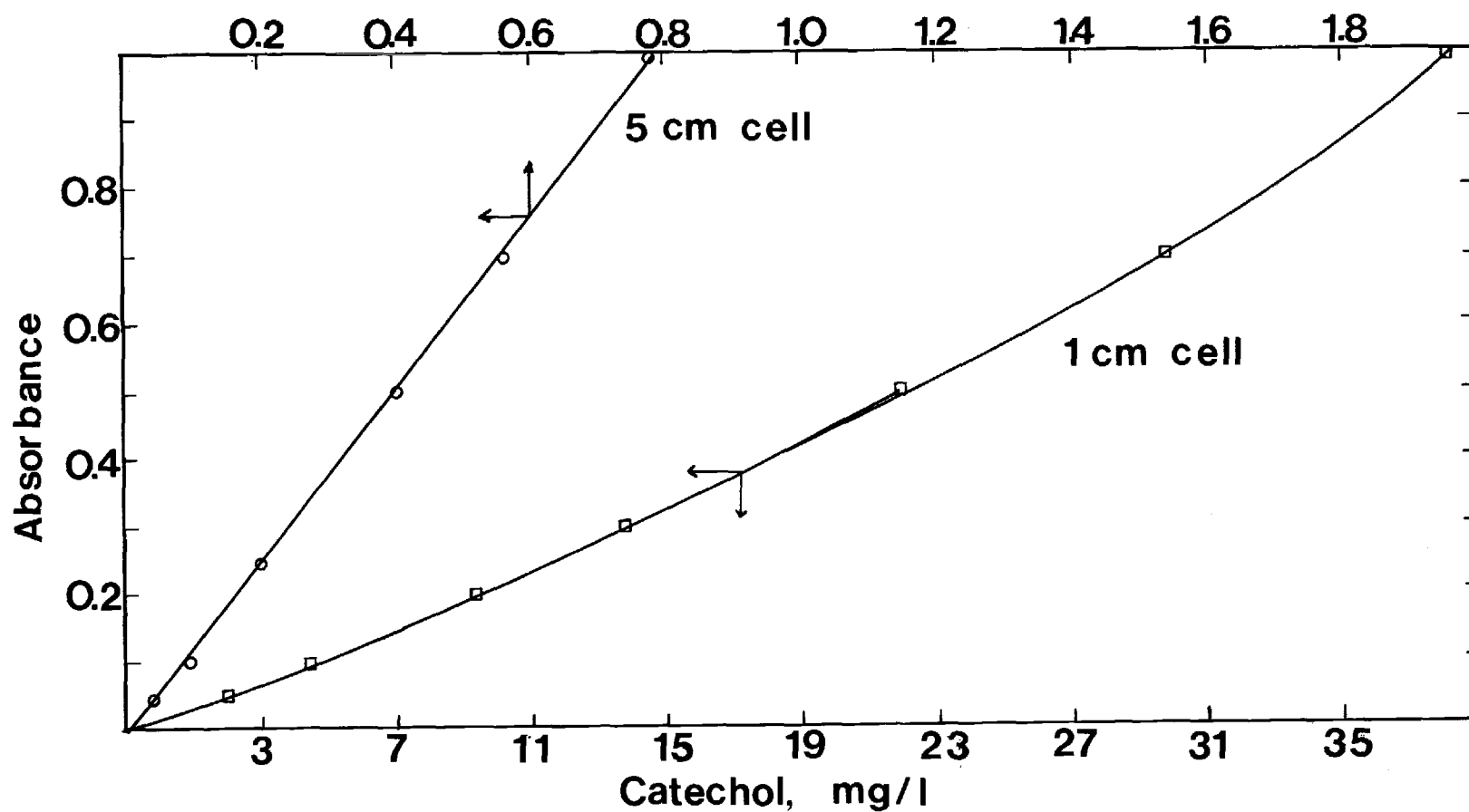
- (a) Total Suspended Solids
- (b) Volatile Suspended Solids
- (c) Alkalinity
- (d) Ammonia Nitrogen
- (e) Total Kjeldahl Nitrogen (TKN)
- (f) Total Inorganic Phosphate
- (g) Oxidation Reduction Potential (ORP)

In addition, analyses were made to determine the ability of the microorganisms within the system to utilize hydrogen and aqueous carbon dioxide to form methane.

Analytical Methods

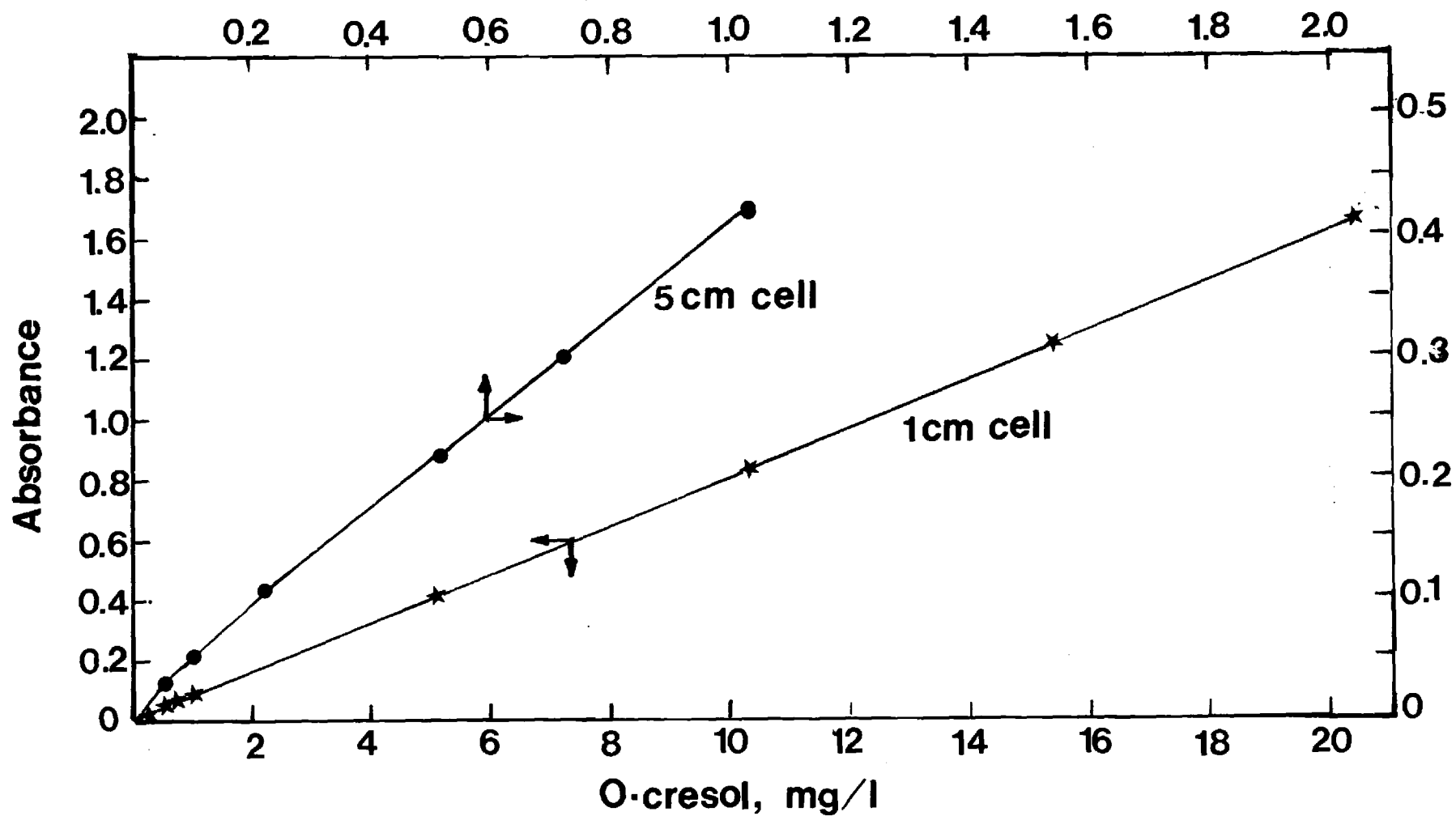
pH. The pH of the liquid effluent was measured immediately after sample withdrawal using a Fisher Accumet pH Meter, Model 144. Immediate readings were found to be necessary in order to insure against any shift in pH due to the loss of dissolved CO₂ to the atmosphere.

Total Inorganic and Organic Carbon. The total inorganic carbon (TIC) and total carbon (TC) content of the influent substrate and effluents from all columns was monitored using a Beckman Model 915 Total Organic Carbon Analyser.



CALIBRATION CURVE FOR CATECHOL

FIGURE 10



CALIBRATION CURVE FOR O-CRESOL DETERMINATION

FIGURE 11

All samples were filtered through 0.45 μ m Gelman Metrical membrane filters prior to analysis. The total organic carbon (TOC) content of the samples was subsequently determined as the difference between the TC and TIC.

Chemical Oxygen Demand. The chemical oxygen demand (COD) of the organic matter present in the feed and effluents from all columns was determined by the Chemical Oxygen Demand Test as described in section 508 of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975). All samples were filtered through a 0.45 μ m Gelman Metrical membrane filter prior to the analysis.

Catechol and o-Cresol Concentration. Catechol and o-cresol concentrations were determined using a Beckman Model 26 Spectrophotometer. All samples were filtered through a 0.45 μ m Gelman Metrical membrane filter prior to analysis. The pH of each sample was adjusted to 12.0 prior to the absorbance determination. This pH value was found to give the highest sensitivity to absorbance at a wavelength of 268 nm for catechol and 235 nm for o-cresol. Standard absorbance versus concentration curves for each of the two phenolic compounds using either 1 cm or 5 cm path length cells are given in Figures 10 and 11. All values are reported in mg/l of catechol or o-cresol.

A Perkin-Elmer Sigma 1 Gas Chromatograph with a Sigma 10 Data System was also utilized to verify the spectrophotometric results. The column used in the analysis was a 183 cm (6 feet) long glass coil with an inner diameter of 2 mm and packed with Carbowax C 60/80 mesh with a stationary liquid phase of 0.5 percent SP1000. The flow rate of the helium carrier gas was set at 30 ml/min. The oven temperature was 250°C while the detector and injection temperatures were 300 and 220°C, respectively. A flame ionization detector was used and air and hydrogen flow rates were maintained at 240 and 40 ml/min, respectively.

Standards and samples were prepared for gas chromatographic analysis according to the following procedure:

- (a.) Use a standard or sample of volume equal to 50 ml.
- (b.) Raise the pH of the sample to 12 in order to insure the complete ionization of the phenols. This high pH was achieved by dropping a pellet of sodium hydroxide in the sample.
- (c.) Place the sample in a separatory funnel and add 50 ml of methylene chloride (CH_2Cl_2) to the separatory funnel and shake vigorously for one minute. Allow time for phase separation and discard the lower CH_2Cl_2 fraction while retaining the upper water portion. Repeat this procedure twice by adding 25 ml portions of methylene chloride.
- (d.) Adjust the pH of the resulting water fraction in the separatory funnel to pH 2 using concentrated hydrochloric acid.
- (e.) Add 50 ml of CH_2Cl_2 to sample in the separatory funnel and shake vigorously for one minute. Allow time for phase separation and retain the lower CH_2Cl_2 fraction. Repeat twice with additional 25 ml portions of CH_2Cl_2 . Combine the CH_2Cl_2 portions and discard the water portions.
- (f.) Concentrate the resulting 100 ml of methylene chloride to 5 ml by removing the solvent in a Kuderna-Danish Concentrator system.
- (g.) One microliter of the extracted and concentrated sample is injected in the injector of the gas chromatographic system.

Catechol exhibited extreme insensitivity to this extraction and concentration procedure. Irreproducible and strongly tailing peaks were obtained for the higher (100 mg/l) as well as the lower (1 mg/l) concentrations. The extraction procedure for catechol was then modified by eliminating steps b and c and concentrating the sample down to 1 ml volume in step f. Once more, however, no improvement in sensitivity or reproducibility was obtained. Efforts are still underway at the present time to develop an improved detection procedure

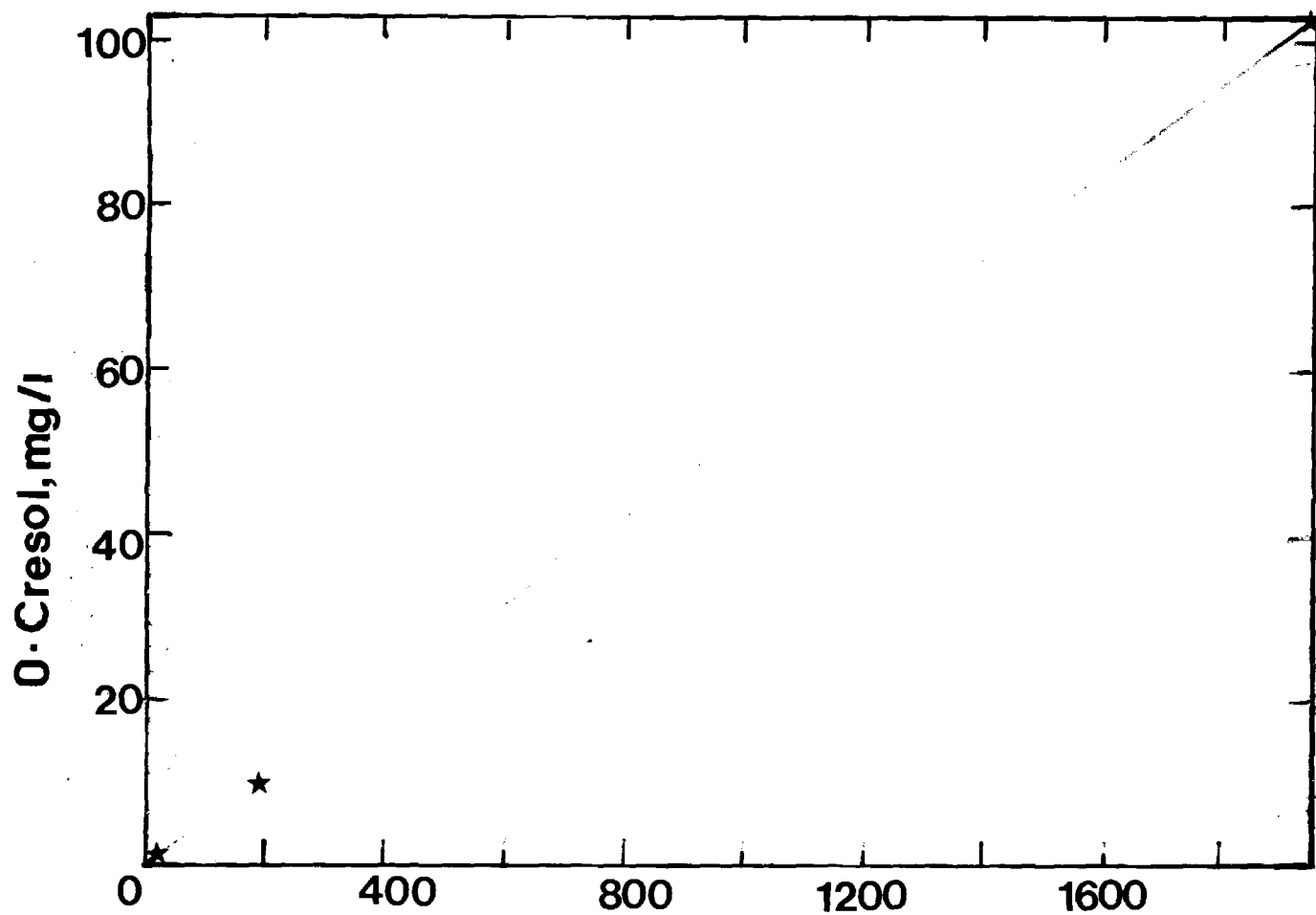
for catechol.

The refined extraction and concentration procedure was used in the gas chromatographic analysis for o-cresol. This procedure gave excellent sensitivity and reproducibility and a consistent retention time of 7.77 minutes in the column. The results obtained from the gas chromatographic analysis agreed very well with those obtained from the spectrophotometric analysis for the lower concentration range. However, for the higher concentrations of catechol obtained in the effluents from the first two columns, the spectrophotometric readings were consistently higher than those obtained from the gas chromatographic analysis, indicating the possibility of spectrophotometric interference from other organic compounds at the wavelength of absorbance. A typical gas chromatographic calibration curve for the o-cresol is given in Figure 12.

The aminoantipyrrene chloroform extraction method for the analysis of phenols as described in section 510 B of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975), was also tried for the analysis of catechol. Once again, however, this method was found to be analytically insensitive in the determination of catechol.

Volatile Fatty Acids. The volatile fatty acids (acetic, propionic and butyric acids) were analyzed for in the filtered samples using a Hewlett Packard F&M Scientific 700 Laboratory Chromatographic system. All values are reported in mg/l as acetic acid.

The Gas Chromatographic Column used in the analysis was a 183 cm (6 feet) long aluminum coil with an inner diameter of 0.32 cm (0.125 inch) and packed with 15 percent SP-1220, 1 percent H_3PO_4 , 100/120 Mesh Chromosorb W/A/W nitrogen was used as the carrier gas at an average flow rate of 30 ml/min. An air to hydrogen ratio of 10 to 1 was maintained. The detector temperature was maintained



Area Under Curve
CALIBRATION CURVE FOR O-CRESOL DETERMINATION
BY GAS CHROMATOGRAPH

FIGURE 12

at 185°C while the injector and column temperatures were held at 180 and 140°C, respectively. Filtered undiluted samples were injected directly into this chromatographic system. Standard solutions of acetic, propionic and butyric acids were used for calibration.

Total and Volatile Suspended Solids. The suspended solids content of the samples was determined using Gooch crucibles and glass-fiber filters as described in section 208 D of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975). In this analysis the required volumes of samples were added to preweighed crucibles and filtered under vacuum. The crucibles were then placed in a 103°C oven for a period of one hour. After this period, the crucibles were removed and cooled in individual desiccators for over 2 hours and weighed again for the determination of total suspended solids. The total volatile solids were determined by placing the cooled crucibles in a muffle furnace at 550°C for a period of 30 minutes, cooling them in individual dessicators for a minimum of 2 hours and reweighing.

Alkalinity. Alkalinity determinations were made on all influent and column effluents according to the procedure described in section 403 of Standard Methods for the Examination of Water and Wastewater, Fourteenth Edition (1975). Instead of using methyl orange as an end point indicator, however, the titration was assumed to be complete at pH 3.7. The sulfuric acid titrant had a normality of 0.12 N. The volume of the titrated sample was 50 ml. Samples were titrated immediately after withdrawal in order to avoid the loss of CO₂ upon exposure to the atmosphere. All alkalinity values were reported in mg/l as CaCO₃.

Ammonia Nitrogen. Ammonia nitrogen determinations were made on the filtered samples using the Technicon Corporation Industrial Method 19-69W. The automated procedure for the determination of ammonia in water using

the Technicon AutoAnalyzer Proportioning Pump in conjunction with a Technicon AutoAnalyzer Sampler and Recorder utilizes the Berthelot reaction in which the formation of a blue-indophenol complex occurs when the ammonium bearing solution is added to sodium phenoxide followed by the addition of sodium hypochlorite (Ferrari, 1960). A solution of potassium sodium tartarate (Rochelle Salts) is added to the sample stream to eliminate the precipitation of the hydroxides of any heavy metals which may be present.

An aqueous solution of ammonium chloride was used to obtain standard calibration curves for this analysis. These standards were prepared on the day of analysis using serial dilutions to obtain concentrations ranging from 0.03 mg/l to 3 mg/l.

Total Kjeldahl Nitrogen. The Technicon Corporation Industrial Method 30-69A was utilized in monitoring the total Kjeldahl nitrogen (TKN) content of the samples. This procedure involved the digestion of the organic material using the Technicon Continuous Digester. The ammonia thus released was quantitatively measured using the Berthelot reaction described previously.

Total Inorganic Phosphate. The determination of the total inorganic phosphate in the liquid samples was done using the Technicon Corporation Industrial Method 4-68W. The total inorganic phosphorus is first converted to the orthophosphate form by hydrolysis with sulfuric acid. The addition of aminonaphthol sulfonic acid reduces the phosphomolybdic acid produced in order for the phosphate concentration to be measured (Lundgren, 1960).

Aqueous solutions of anhydrous potassium dihydrogen phosphate were used to generate standard calibration curves in the concentration range of 0 - 40 mg/l - P.

Oxidation Reduction Potential. A 70 cc continuous flow through cell having three parts was designed for the measurement of the insitu oxidation

reduction potential (ORP). A platinum combination electrode connected to a Fisher Accumet pH Meter, Model 144, was inserted tightly in the continuous flow cell. The other two parts of the cell were connected to the two T-connections on the recirculation line of the column under consideration using Tygon tubing. The flow through cell was filled slowly in an upright manner to avoid any oxygen contamination and once filled and sealed, the recirculated flow was completely diverted through the cell and the ORP was recorded when the reading was stabilized. All ORP values are reported versus a saturated calomel reference electrode.

Gas Analysis. Gas samples were analyzed for methane, carbon dioxide, nitrogen and oxygen using a Fisher Gas Partitioner Model 25V in conjunction with a Fisher Thermal Stabilizer Model 27 and a Coleman Recorder, Hitachi 165. Helium was used as the carrier gas. Analysis for hydrogen was accomplished using a Fisher Gas Partitioner Model 25V with argon as the carrier gas. Certified Calibration Standards (Matheson, East Rutherford, NJ) were used to calibrate the gas analyzer.

The helium carrier column was a 76.20 cm (30 inch) long aluminum column with a 0.64 cm (0.25 inch) outer diameter. This column was packed with 30 percent diethylhexylsebacate on 60 x 80 mesh Columnpak. This column was followed by a 183 cm (6 feet) long 0.476 cm (0.1875 inch) outer diameter aluminum column packed with 5A Molecular Sieve 60 x 80 mesh. The helium gas flow rate was set at 80 ml/minute.

The argon carrier column had identical dimensions and the same molecular sieve packing as the helium carrier column. In this case, however, the first column was packed with 30 percent hexamethylphosphoramide on 60 x 80 mesh

Columnpak. The argon gas flow rate was set at 80 ml/minute.

Hydrogen Utilization and Methane Formation. Anaerobic pure culture investigations have demonstrated that hydrogen appears to be the only universal substrate for all methanogens. Based on this fact, Hudson (1979) developed a test whereby a biomass bearing sample (either in solution or attached to medium granules) is placed in an environment of hydrogen gas and a carbonate bearing substrate for a period of 84 hours. The quantity of methane gas produced in the vial by the end of the incubation period is then taken as a relative measure of the methanogenic activity within the sample.

The experimental protocol employed involved the maintenance of strict anaerobic conditions in the inoculation of a series of 22 ml vials with the following:

- (a.) 7 ml of a prereduced nutrient-bicarbonate medium (see Table 14). This medium is essential as the micro-organisms effecting hydrogen metabolism must be restricted only by that substrate. The bicarbonate salt provides the source of electron acceptors for the production of methane.
- (b.) 7 ml of an anaerobic culture or a few granules of activated carbon were then added to the vial while maintaining a nitrogen atmosphere within the vial.
- (c.) The vials were then sealed with serum stoppers designed for syringe applications.
- (d.) The head space and aqueous phase within the vials was then purged with hydrogen gas for a period of 2 minutes in order to completely displace the original head space gas.
- (e.) After flushing with hydrogen gas, the vials were mounted on a slowly revolving rack to insure mixing and this rack, along with the vials, was incubated for a period of 84 hours at 37°C.
- (f.) After incubating, the vials were allowed to stand for 1 hour at room temperature prior to gas analysis.

- (g.) The head space of each vial was then brought to a pressure of 1 atmosphere using degassed distilled water. The distilled water was introduced into the vial using a syringe and the volume of distilled water added was measured and recorded.
- (h.) Once the head space pressure was equilibrated with the atmospheric pressure, the head space gas was analyzed for methane, carbon dioxide, hydrogen, and nitrogen.

Table 14. Composition of Vial Test Medium

<u>Compound</u>	<u>Quantity</u>
NH ₄ Cl, g	0.6
KH ₂ PO ₄ , g	1.0
K ₂ HPO ₄ , g	2.0
MgCl ₂ · 6H ₂ O, g	20.0
CoCl ₂ · 6H ₂ O, g	10.0
CaCO ₃ , g	1.0
NaHCO ₃ , g	5.3
Vitamin-mineral (dry), g	0.5
Cysteine Hydrochloride Solution, ml	5.0

Make up to 1 l with distilled water, mix, settle and then decant the supernatant. Add 1 ml of 0.01 g/l Resarazin to supernatant.

Electron Micrography. Electron microscopic observations were made on the virgin and biologically coated carbon granules, using a Cambridge Instrument Stereoscan Mark II A Electronmicroscope. The granules were first washed and freeze dried. Individual carbon granules were then placed onto glass slides which were subsequently placed on a brass block in liquid nitrogen for freezing the granules on the glass slides. The slides were then placed in a vacuum chamber to complete the drying process. The granules were then placed on slides which were previously painted with a silver conducting paste. The slides were then placed in the vacuum chamber and a thin layer of gold-palladium was plated onto the granule surface.

RESULTS AND DISCUSSION

The two anaerobic-activated carbon filter systems, employed in this study, were operated using catechol and o-cresol as the major sources of organic carbon in the synthetic feed substrates. An additional source of organic carbon in the feed substrates was due to the ethanol, sodium citrate and vitamin extract content of the salt solution. The COD of the stock salt solution averaged around 25,668 mg/l while the TOC was 6,643 mg/l giving rise to a COD to TOC ratio of 3.86. The data in Table 15 give the contribution to COD and TOC of one gram of catechol and o-cresol.

Table 15. COD and TOC Contribution of Catechol and O-Cresol

Compound	Molecular Weight (g)	Contribution of 1 g of Organic Compound	
		COD (g)	TOC (g)
Catechol	110	1.8909	0.6545
O-Cresol	108	2.5185	0.7778

Treatment of Catechol Bearing Substrate

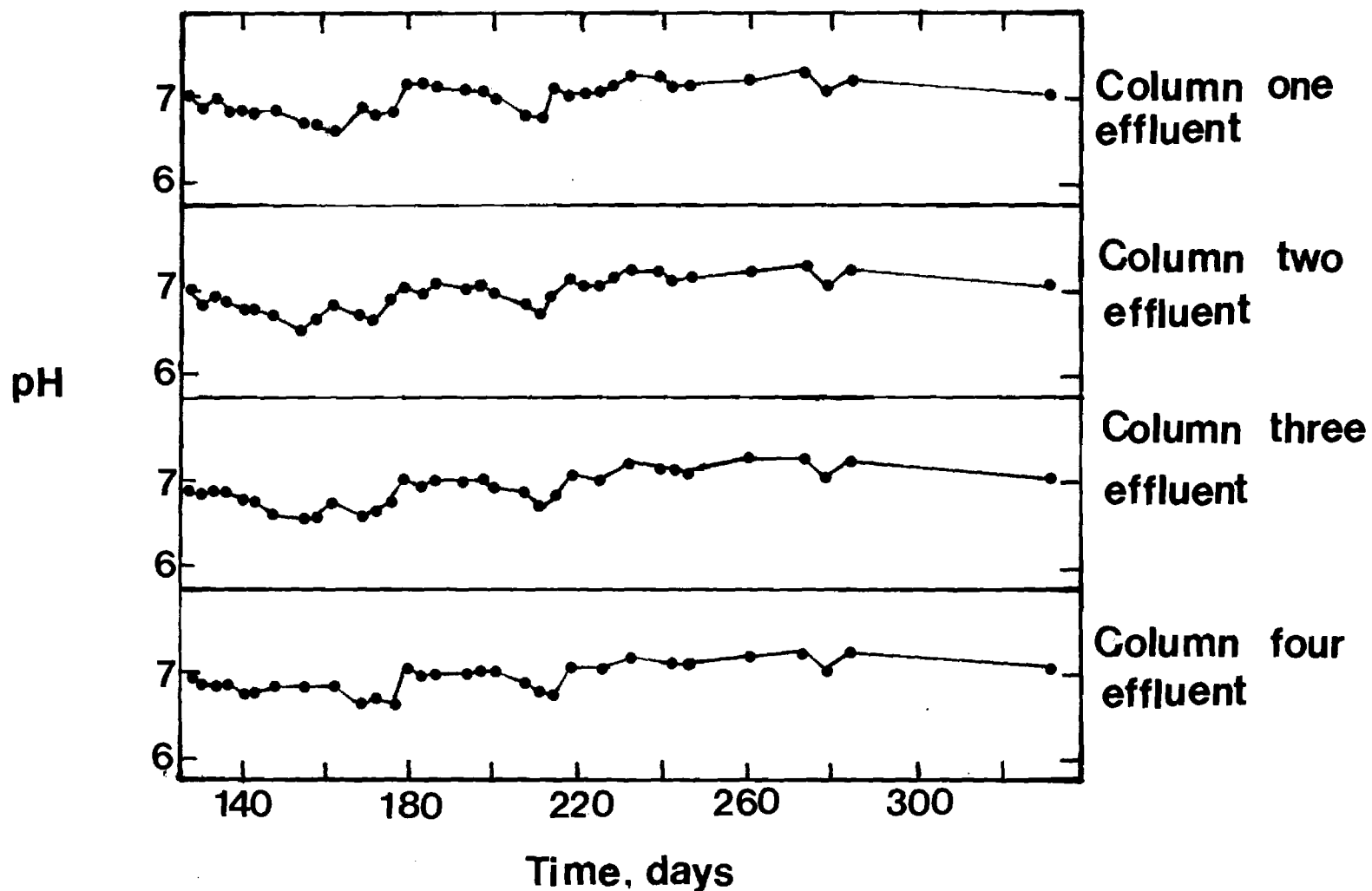
The catechol fed experimental reactor was operated continuously for a period of 557 days. During the first phase of this experiment, which extended over a period of 333 days, the feed catechol concentration was maintained at 200 mg/l, while in the second phase of the experiment, which lasted for 178 days, the catechol concentration in the synthetic feed was increased to 400 mg/l. During the third and last phase of this experiment, the system performance was tested against a feed catechol concentration of 1000 mg/l for a period of 47 days.

Phase I, 200 mg/l Catechol

During this phase of the catechol degradation experiment, the feed substrate was prepared daily in 4 l batches using 14 ml of the salt solution,

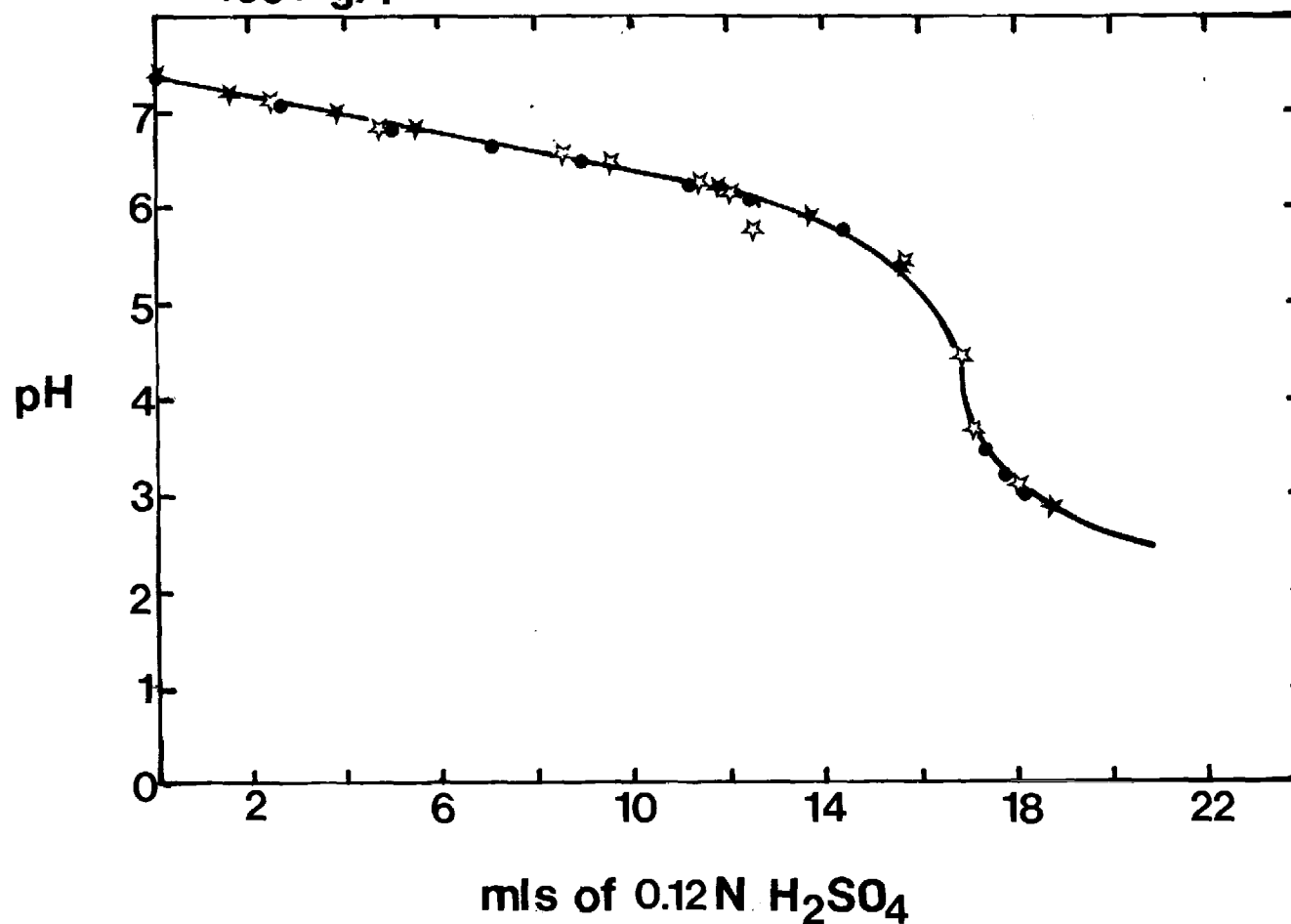
80 ml of the phosphate buffer solution, 0.8 g of catechol and distilled water. The theoretical feed COD and TOC computed using the measured values for the salt solution and the theoretical values for catechol given in Table 15 were 468 and 154 mg/l, respectively. The measured values of the two parameters COD and TOC in the feed as obtained from the average of 28 duplicate readings were 414 and 139 mg/l, respectively. These computations and measurements yield a computed COD to TOC ratio of 3.04 and a measured ratio of 2.98. During the initial period of study, the pH of the feed substrate was varied in an attempt to establish an operating pH within the four columns ranging between 6.9 and 7.1. Once the acclimation period was over, the pH of the feed substrate was maintained at 7.4. This resulted in a pH distribution through the treatment system ranging between 7.03 and 7.35. The pH values in the individual column effluents during the course of this phase of the experiment are given in Figure 13. The titration curve of the feed substrate shown in Figure 14 indicates the synthetic waste to have a strong buffer capacity of 0.91 meq of acid in the pH range of 7.4 down to the lowest pH recorded in the column effluent of 6.59. This strong buffer capacity coupled with the buffer intensity of the recirculated flow of 50 ml/min was sufficient to maintain the system pH close to the neutral pH of 7 throughout the experiment (Chian and DeWalle (1976), Witt et al. (1979)).

During the first phase of this experiment the first column was observed to go through four distinct stages of activity. During the first stage, which lasted for 120 days of continuous feeding, no appreciable gas production was observed from this system. This was due to the adsorption of the catechol onto the activated carbon surface thus rendering the substrate unavailable for biodegradation by the microbial culture. The second stage of this phase



I. pH IN INDIVIDUAL COLUMN EFFLUENTS FROM CATECHOL FED REACTOR
FIGURE 13

☆ 200 mg/l
★ 200 mg/l
● 400 mg/l



BUFFERING CAPACITY OF CATECHOL INFLUENT FEED

FIGURE 14

of the experiment, which lasted for 25 days, was characterized by acclimation and the initiation of gas production. Data collected during this stage of the experiment show a definite decrease in the organic content of the column effluents. The next distinct experimental stage observed was characterized by an accelerated biological activity and the bioregeneration of the activated carbon. During this stage of the experiment, which lasted for 85 days, the carbon equivalent of the gaseous products (methane and aqueous as well as gaseous carbon dioxide) exceeded the organic carbon removed by the process thus indicating the utilization of some of the previously adsorbed organic carbon, or bioregeneration. After this transient period had subsided, gas production decreased to a level which corresponded very closely to the organic carbon removed across the treatment process thereby signifying steady-state operating conditions.

Catechol Reduction. The concentration of catechol measured in the effluents from the four anaerobic activated carbon columns connected in series is shown in Figure 15. During the first 50 days of continuous operation very little catechol was detected in the effluent from the first column. This was due to the removal of the dihydroxyphenol from solution by adsorption onto the carbon surface. After this initial period, the concentration of catechol in the effluents of the first two columns began to increase reaching a high of 140 mg/l in the effluent of the first column and 11 mg/l in the effluent of the second column on the 120th day of continuous feeding. At that time gas production was observed from the first two columns and the concentration of catechol in the effluents of the first two columns began to decrease. After day 225 the performance of the column, as determined by catechol reduction, reached a stage of steady state performance. However, as will be shown

I. CONCENTRATIONS IN INDIVIDUAL COLUMN EFFLUENTS FROM CATECHOL FED REACTOR

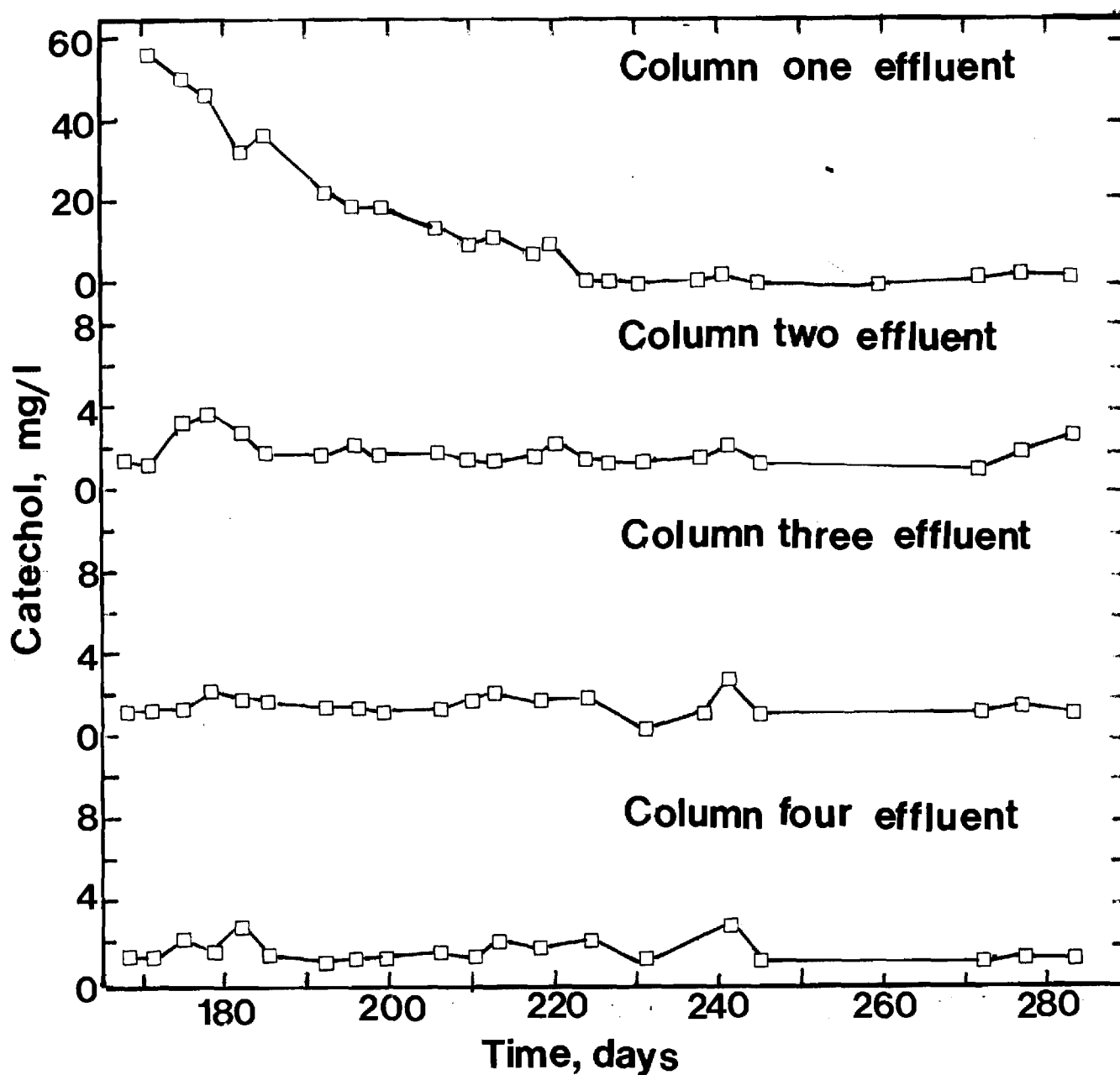


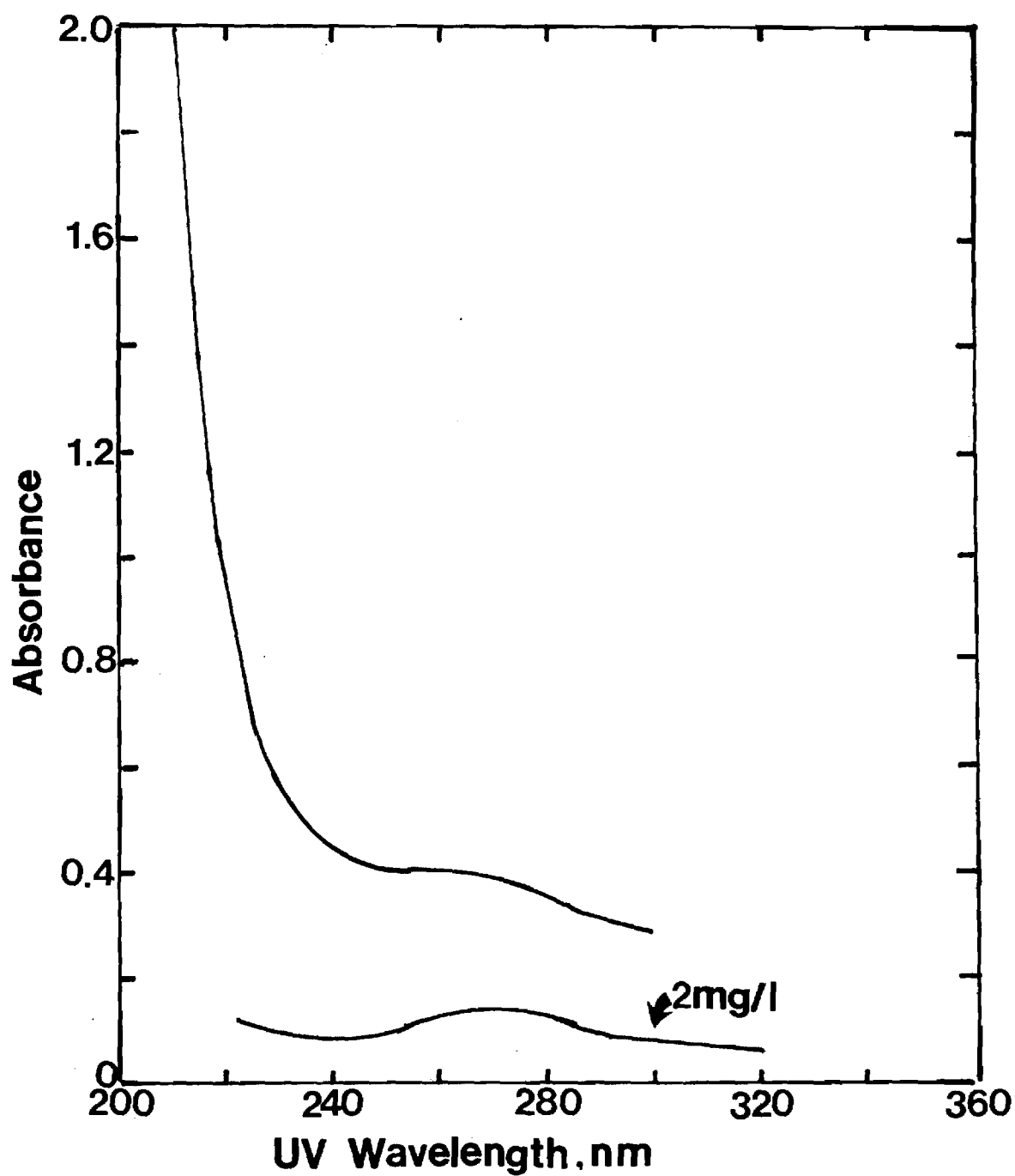
FIGURE 15

later in the case of gas production, true steady state conditions were not established until day 240 of continuous operation.

After day 225, the catechol content in the effluent from the first column was consistently lower than 3.6 mg/l. This corresponds to a catechol removal efficiency in the first column of better than 98.2 percent. The concentration of catechol found in the effluent of the second column averaged below 1.9 mg/l for the same period. This corresponds to a cumulative removal of catechol in the first two columns of better than 99.05 percent.

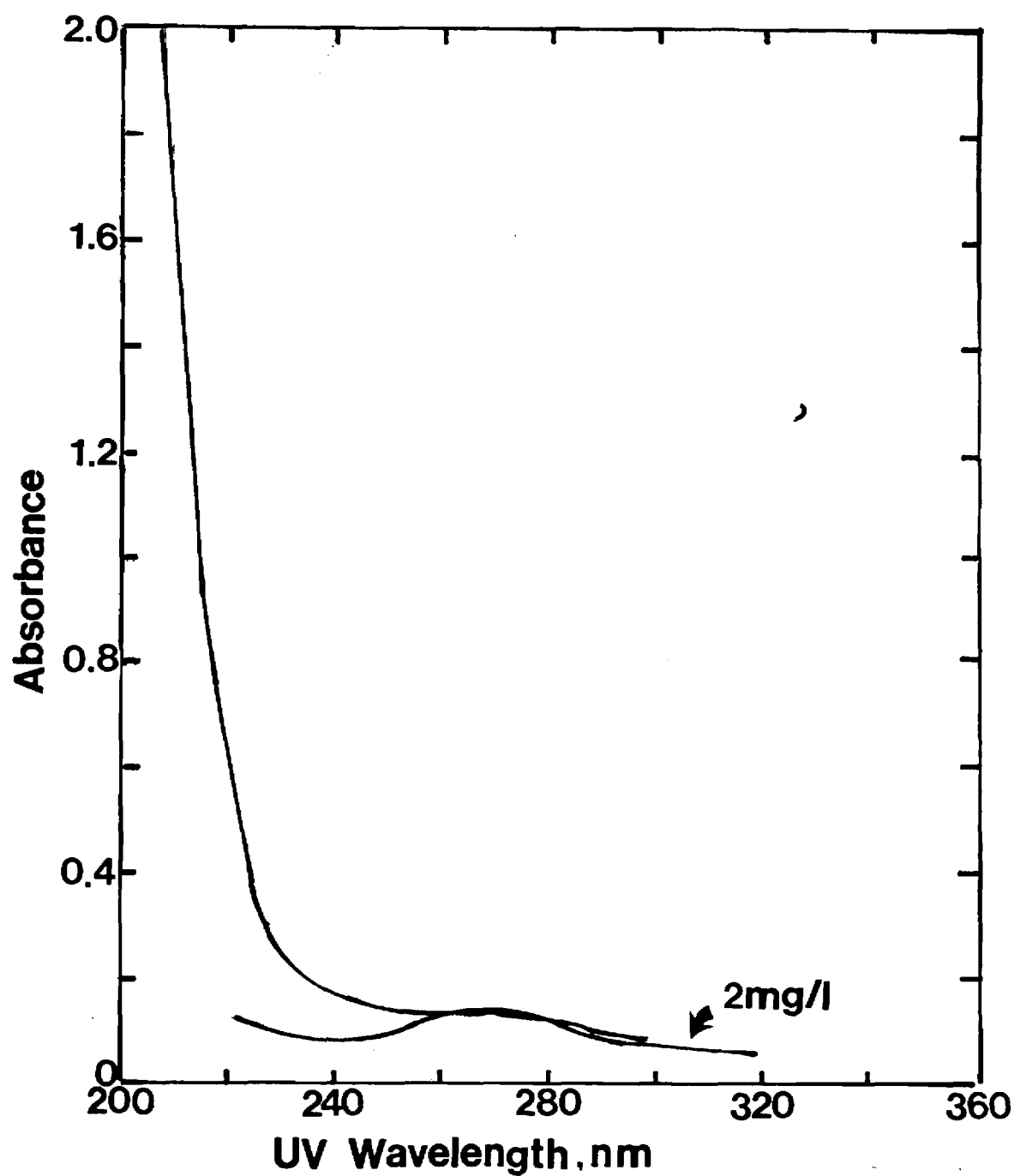
The catechol concentration values reported in Figure 15 are all greater than the actual concentrations of this phenolic compound. This discrepancy in the concentration values of catechol as measured in the column effluents is due to the spectrophotometric analytical method utilized to monitor this compound and the contribution to the absorbance reading of the organic intermediates of catechol biodegradation of 268 nm. To illustrate the interference of other organic matter with the absorbance readings, the absorbance scan of a catechol-distilled water solution at pH 12 was plotted against similar scans conducted on the effluents from the four anaerobic filter columns (see Figures 16, 17, 18 and 19). Examination of these figures shows the absence of a peak in absorbance at 268 nm for the scans on the column effluents while this peak is very pronounced in the scan conducted on the distilled water-catechol solution. Based on these observations, it was concluded that the actual catechol content in the column effluents may very well be below measurable limits, resulting in actual removal efficiencies of this phenolic compound approaching one hundred percent.

Organic and Inorganic Carbon. The organic and inorganic carbon content of the synthetic feed substrate as well as the effluents from the four anaerobic columns is presented in Figure 20 for the period of operation



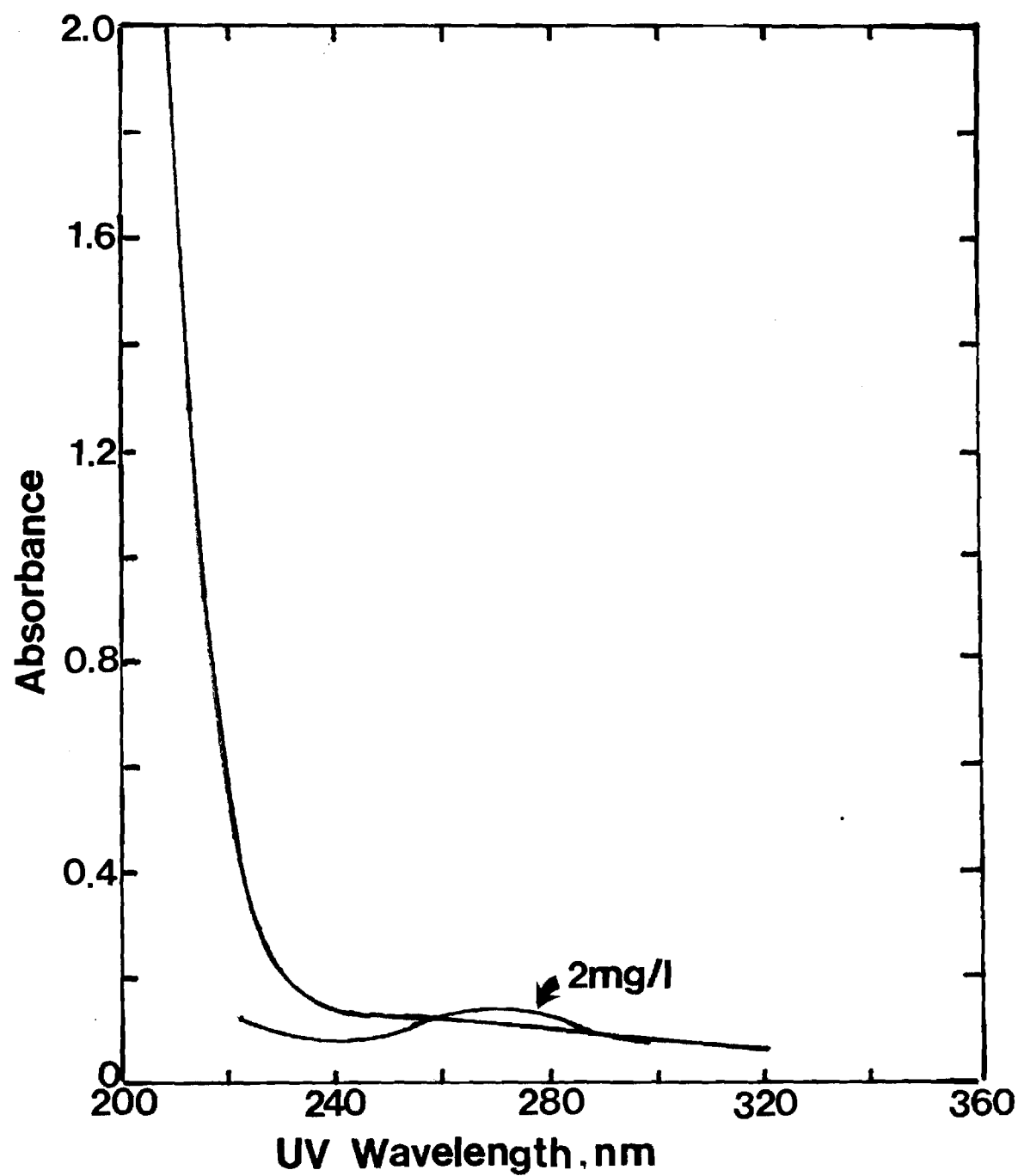
TYPICAL SPECTROPHOTOMETRIC SCAN OF
CATECHOL ONE

FIGURE 16



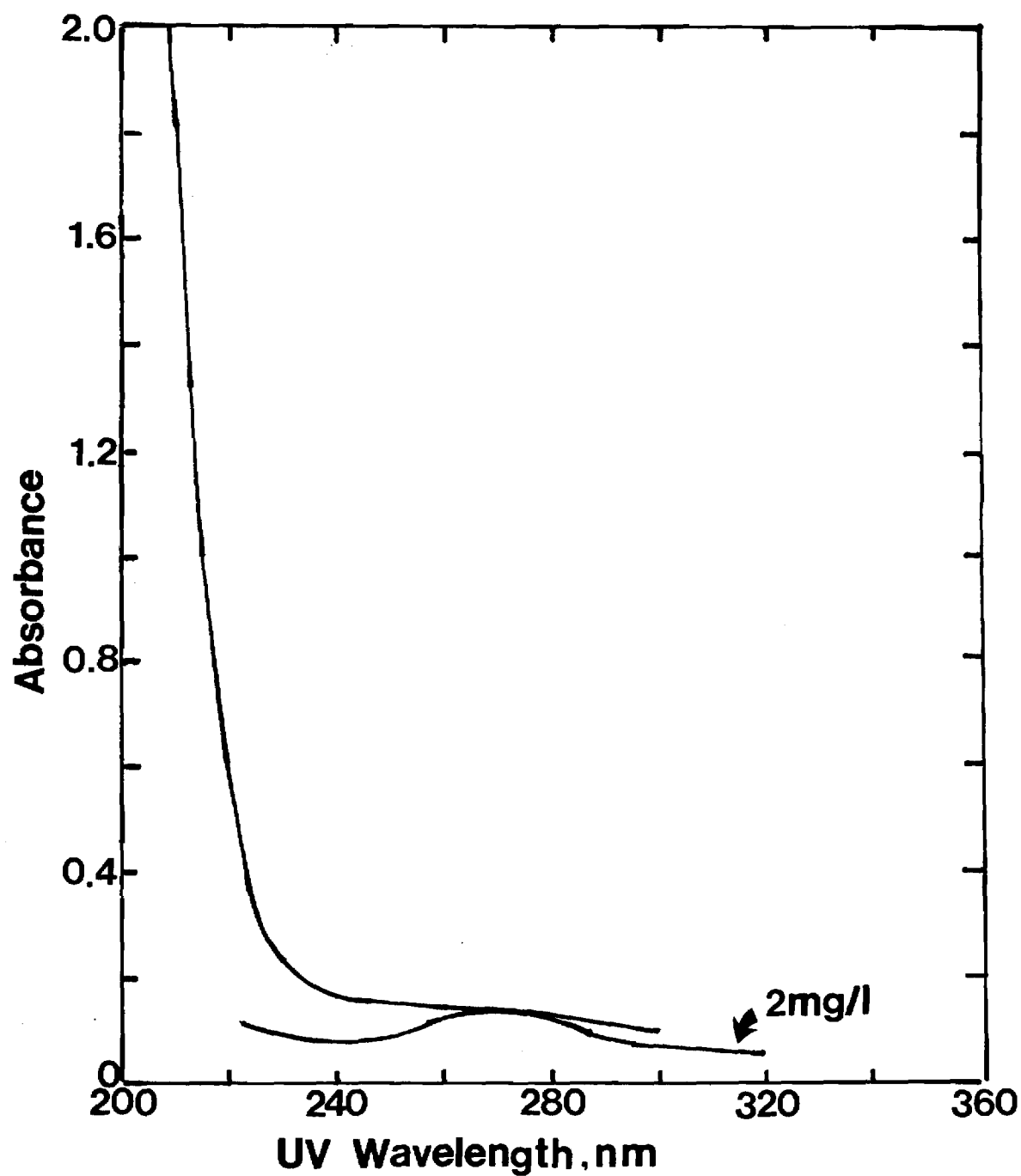
**TYPICAL SPECTROPHOTOMETRIC SCAN OF
CATECHOL TWO.**

FIGURE 17



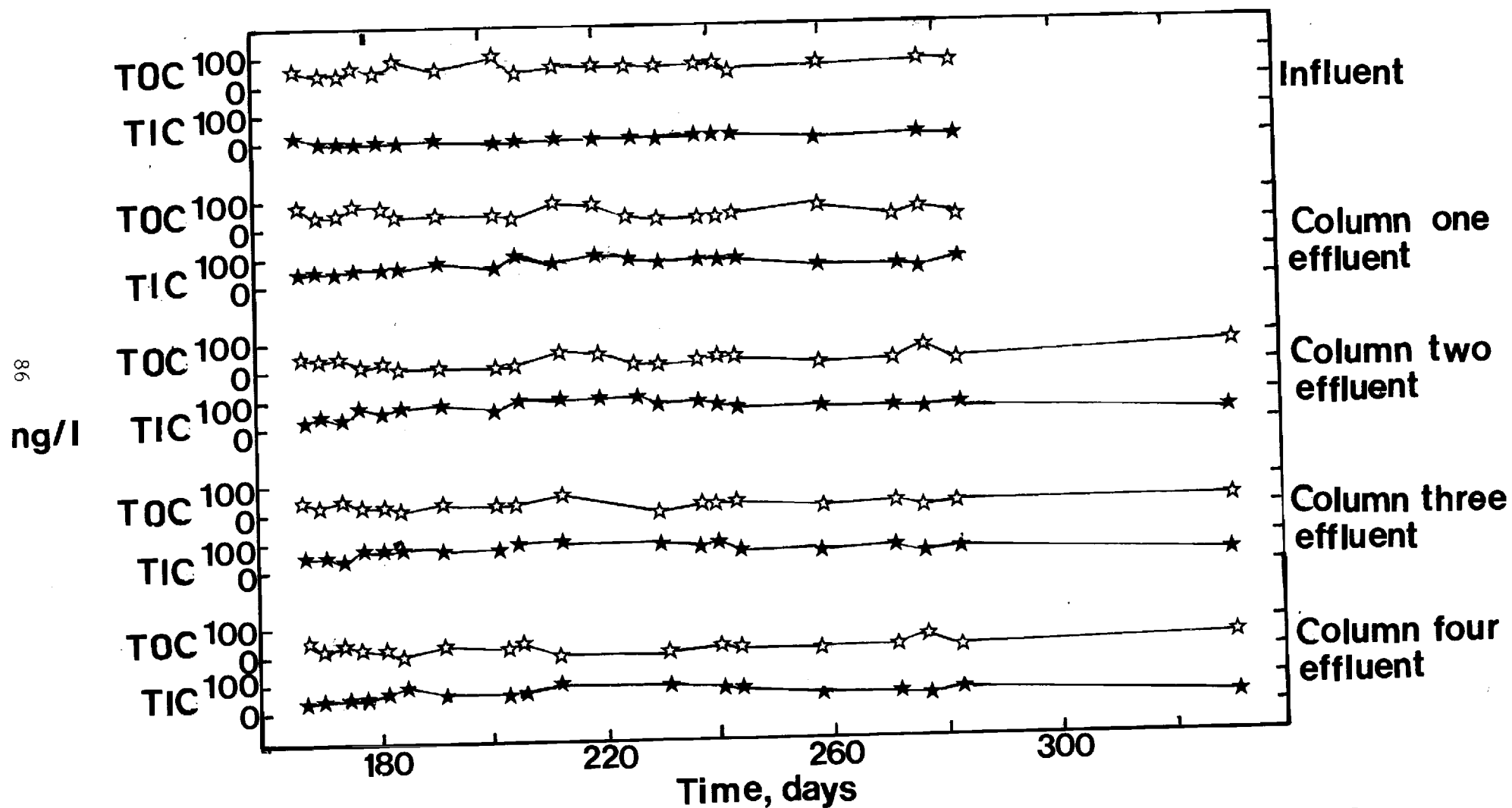
**TYPICAL SPECTROPHOTOMETRIC SCAN OF
CATECHOL THREE**

FIGURE 18



**TYPICAL SPECTROPHOTOMETRIC SCAN OF
CATECHOL FOUR**

FIGURE 19

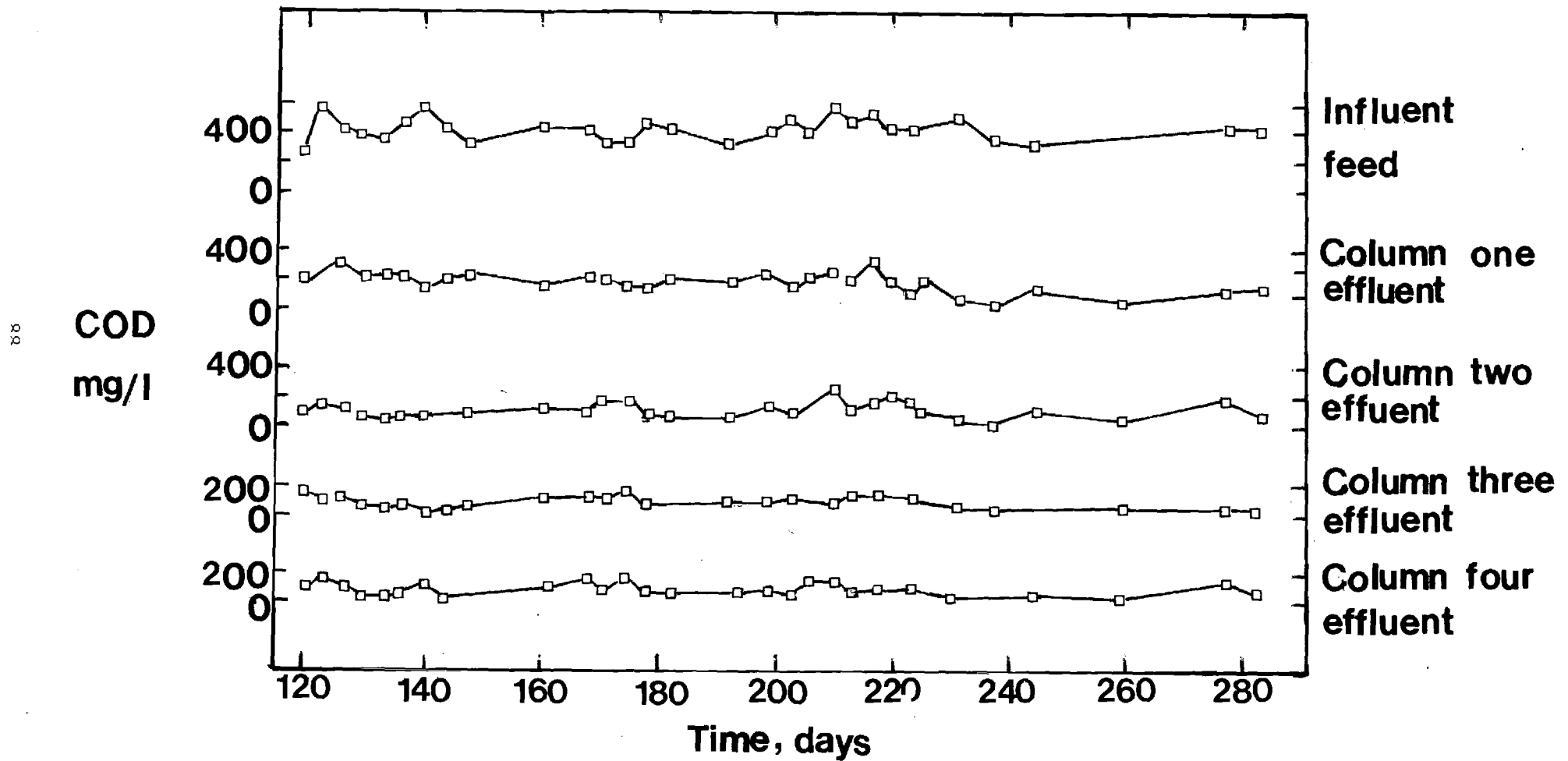


I. TOC AND TIC CONCENTRATIONS IN INDIVIDUAL COLUMN EFFLUENTS FROM
CATECHOL FED REACTOR
FIGURE 20

extending between days 168 and 330. The average TOC in the feed was 139 mg/l while the organic carbon content of the effluent from the first column decreased from 88 mg/l on day 168 to 26 mg/l on day 330. The organic carbon content of the effluents from the last three columns decreased from 47, 37 and 57 mg/l on day 168 to 25, 24 and 22 on day 330. The low organic carbon content present in the effluent from the first column during steady state operating conditions signifies the starved conditions under which the last three columns were operated during this phase of the experiment. This serves to emphasize the fact that a single activated carbon packed anaerobic filter, having an empty bed detention time of 11.62 hours would have been sufficient in treating a 200 mg/l catechol bearing synthetic substrate.

The inorganic carbon content of the waste (see Figure 20) increased as the organic carbon content of the solution decreased due to the dissolution of carbon dioxide into the aqueous phase. Carbon dioxide and methane gas represent the major end products of the anaerobic degradation of catechol and the dissolution of the former in the aqueous stream results in the production of a methane rich gas phase. The monitoring of the inorganic carbon content of the aqueous phase is essential in that it provides a means for establishing a material balance as to the fate of the carbon content of the feed wastewater. The average steady state inorganic carbon content of the feed substrate and the effluents from all four columns were 12, 62, 70, 66 and 65 mg/l, respectively.

Chemical Oxygen Demand. The performance of the treatment system as far as chemical oxygen demand removal is presented in Figure 21 for the period extending from day 118 to day 283. Initial COD measurements on day 118 on the effluents from columns 1 through 4 were 183, 72, 109 and 60 mg/l, which



I. COD CONCENTRATIONS IN COLUMN EFFLUENTS FROM CATECHOL FED REACTOR

FIGURE 21

represent percentage reductions in COD of 55.8, 82.61, 73.67 and 85.51, respectively. The COD concentration in the effluents from the four columns continued to decrease until steady state operating conditions were reached where the effluent COD values averaged 50, 50, 40 and 40 mg/l from columns 1, 2, 3 and 4, respectively. These represent steady state removal efficiencies of 87.92, 87.92, 90.34 and 90.34 percent from columns 1, 2, 3 and 4, respectively. The COD data collected on day 118 indicate the first two columns were accomplishing most of the COD removal while the steady-state data, on the other hand points more towards a very active first column while the remaining three columns were, apparently operated under starved conditions.

Volatile Acids. The volatile acids: acetic, propionic and butyric, were all monitored throughout the duration of this phase of the study. During the early stages of this phase of the experiment acetic acid was detected in the effluents of all four columns; however, its concentration was consistently below 25 mg/l (which is below the accurate detection limits of the analytical procedure employed). During the later stages of this phase of the experiment, when the biological activity became limited to the first two columns and later to only the first column, very low volatile acids concentrations were detected throughout the reactor system.

Gas Production. The anaerobic gas produced from every column reactor was collected separately, and monitored for volume and composition. Very little gas production was observed from the reactor system prior to day 94 when all four columns were reseeded using a rich methanogenic culture from a glucose fed laboratory batch reactor. Upon reseeded, gas production was observed from all columns, however, the microbial activity eventually diminished in columns 3 and 4 as a result of the accelerated substrate uptake in columns 1 and 2. Measureable gas production was observed from columns 1 and 2 on

day 116. The cumulative total dry gas production from columns 1 and 2 is given in Figure 22 for column 1 and 23 for columns 2. The total cumulative dry gas production for the whole reactor is presented in Figure 24.

The data in Figure 22 indicate that the first column was dormant as far as gas production during the first 116 days of continuous operation. The first column continued to exhibit a slow rate of gas production through day 135 when the rate of gas release from the first column started accelerating until it reached a maximum rate of 800 ml of methane per day at STP. If all the organic carbon in the feed is converted to methane gas, this would account for 747.26 ml of methane per day at STP. In reality, an appreciable fraction of the organic carbon in the feed is converted to carbon dioxide which appears either in the gas phase or dissolves in the effluent and is recorded as the total inorganic carbon, TIC. Consequently, during the period of accelerated gas production from the first column which extended from day 160 through day 230 of continuous operation, more carbon was produced in the gas phase of column 1 in the form of methane and carbon dioxide than the difference between the total carbon contents of the feed substrate and the effluent from column 1 thus signifying a period of bioregeneration of the activated carbon. This period of accelerated gas production from column 1 subsided, however, on day 230 to a steady production level of 287.5 ml/day of methane measured at STP. This gas production level is shown later to correspond to a steady state production level from the first column.

The rate of gas production from the second column was very similar to that observed from the first column (see Figure 23). Gas production was first observed from this column on day 118 of continuous operation. This slow rate of gas release continued through day 153 after which the rate of gas

I. TOTAL GAS PRODUCTION FROM CATECHOL ONE REACTOR

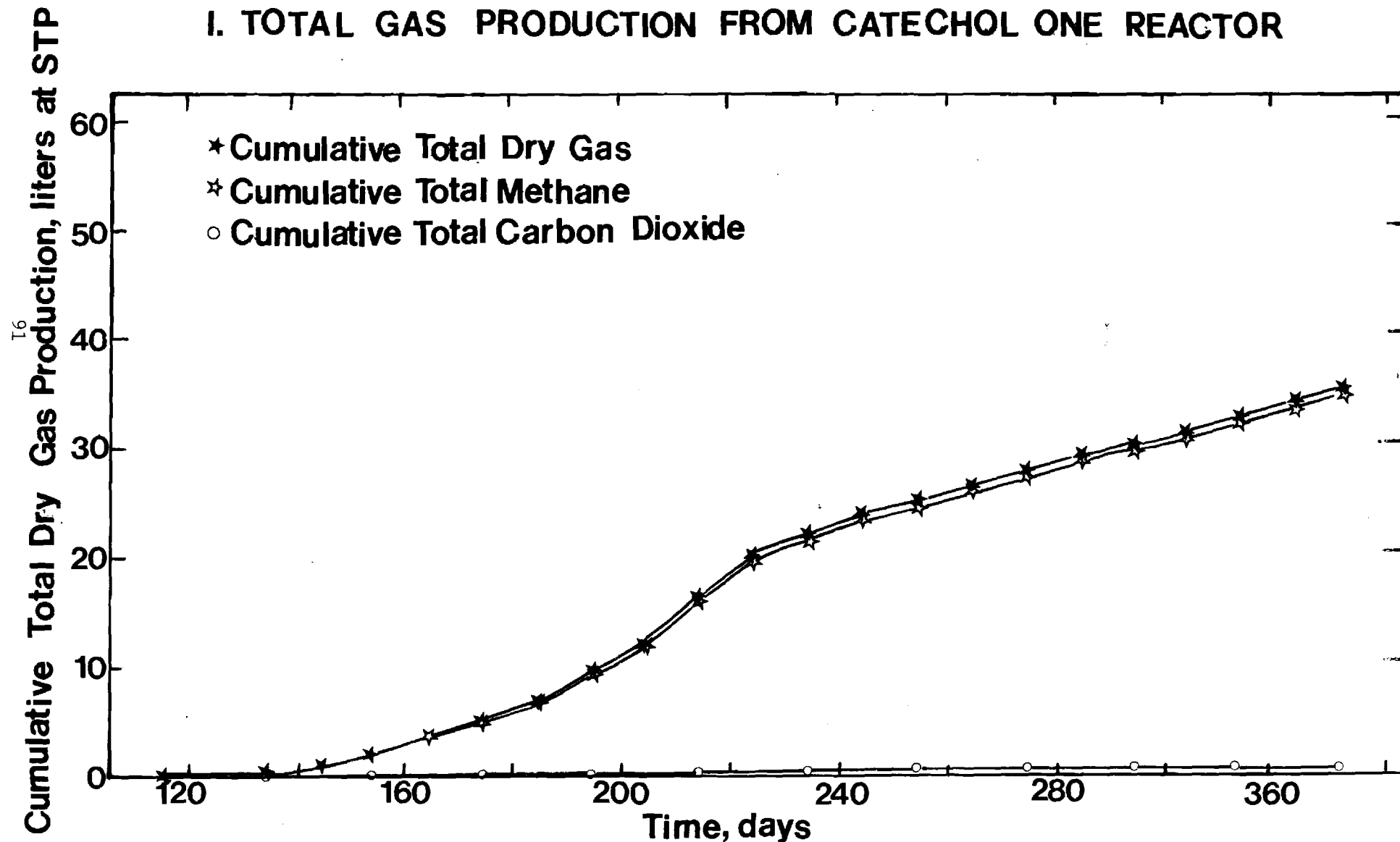
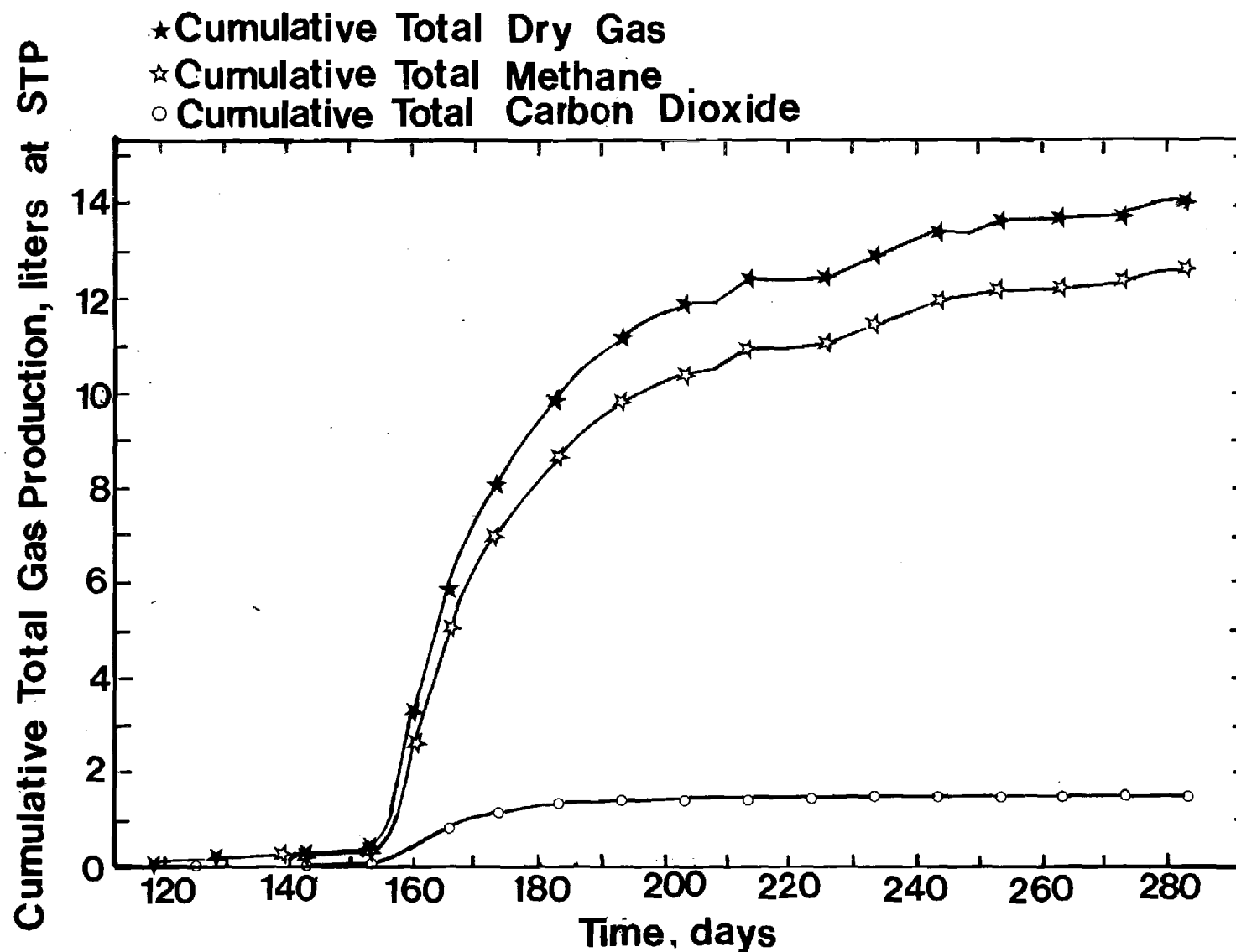
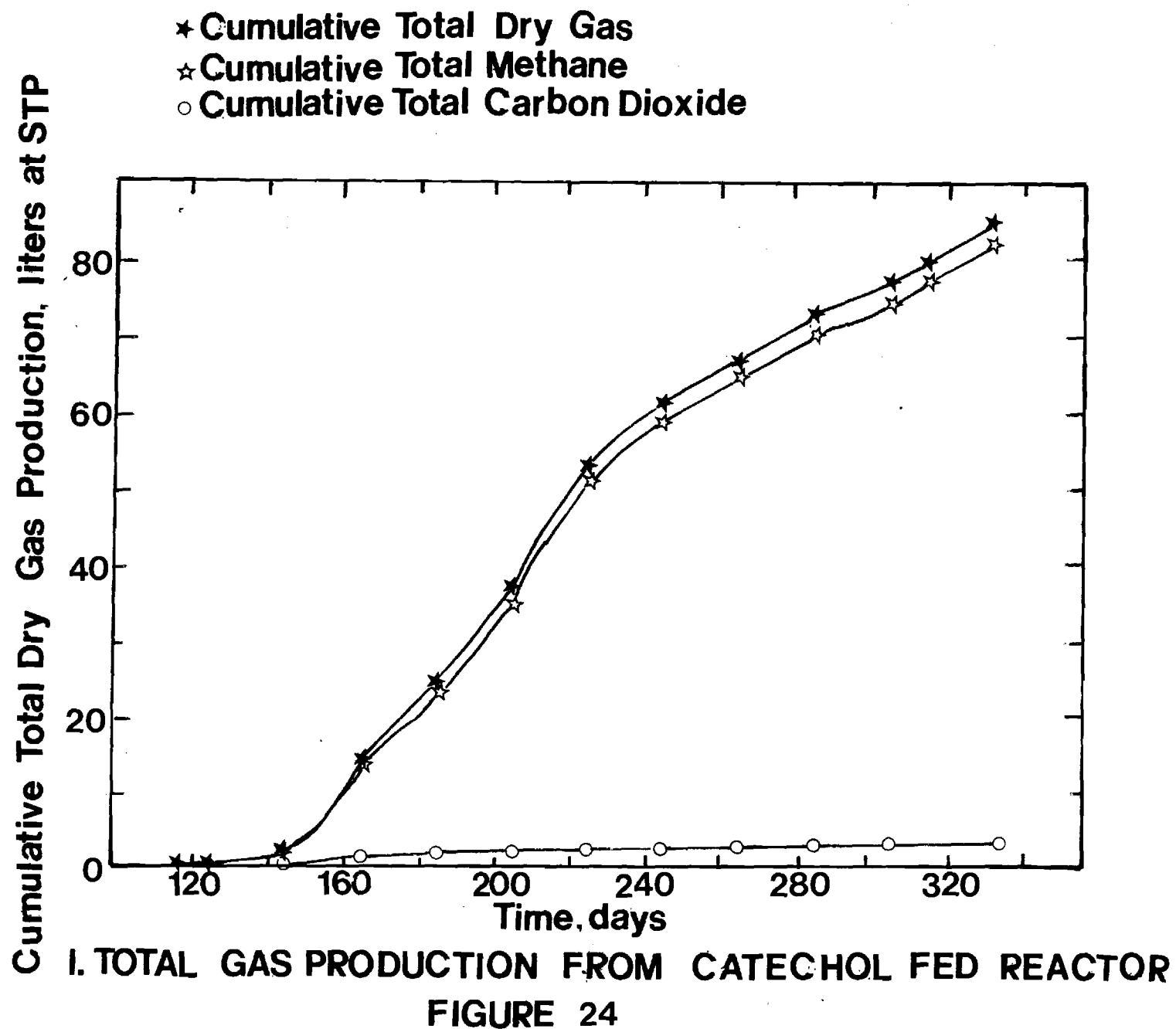


FIGURE 22



I. TOTAL GAS PRODUCTION FROM CATECHOL TWO REACTOR

FIGURE 23



production accelerated sharply through day 190 reaching a peak production level of 600 ml of methane per day on day 160. Once again the volume of gas produced during that period corresponded to carbon than the organic carbon removed in the second column signifying that bioregeneration of the activated carbon is occurring during this period of operation. After this period of accelerated gas production had subsided, the methane production rate from the second column continued at a much slower but "steady" rate of 16.8 ml/day.

The cumulative gas production from the first two columns which effectively represents the total gas production from the reactor system is presented in Figure 24. Once again, the data in this figure illustrate the four stages through which the experimental system has gone through during this phase of the experiment. The period extending from the start of the experiment til day 116 represents a stage where adsorption onto the activated carbon surface was the principal mechanism of removal of catechol, while the stage extending from day 116 to day 145 represents a period of acclimation of the microbial culture to catechol. Bioregeneration of the carbon surface was strongly evidenced during the period extending between day 145 and day 230 while steady state operating conditions were established after day 230. The data in Table 16 represent a summary of the gas production rates and the composition of the anaerobic gas produced during this phase of the study. Note that all gas measurements were reduced to a 100 percent based on the carbon dioxide and methane content only. The rate of production of nitrogen gas in the system was eliminated from the material balances. Nitrogen gas appeared in the anaerobic gas due to the degassification of this element out of solution due to the reduced nitrogen tention in the gas phase as compared to its abundance under atmospheric conditions.

Table 16. Summary of Gas Production and Composition During Phase 1 of the Experiment

Period (days)	Average Reduced Gas Production (ml/day)	Average Methane Production (ml/day)	Actual % Methane	Reduced % Methane
116-140	63.9	62.1	0-47.1	97.2
140-210	562.8	530.6	47.1-97.8	94.3
210-225	680.3	655.7	83.2-84	96.4
225-290	289.4	289.4	78.5-86.2	100.0
290-332	304.3	296.8	76.7-85.2	97.5

In order to better illustrate the different stages that the treatment system experienced during this phase of the experiment, carbon material balances were constructed across the feed substrate and the effluents from all four columns. These material balances are extremely helpful as a tool to better understand the performance of an anaerobic treatment process and help assess its full treatment potential.

The underlying concept behind the construction of such material balances lies in the fact that in an anaerobic environment, the organic carbon content of the feed substrate could either be converted to (a) methane or carbon dioxide gas, (b) dissolved inorganic carbon in the form of aqueous carbon dioxide, or bicarbonate and carbonate ions (c) remain in the unconverted aqueous phase either as the parent feed compound or in the form of some intermediate biological product (d) result in the production of biomass which may remain within the system or escape in the effluent stream and (e) adsorb onto the activated carbon surface which is a unique and special feature of this treatment process. Mathematically, this material balance could be restated as:

$$\text{TOC}_{(\text{in})} + \text{TIC}_{(\text{in})} = \text{TOC}_{(\text{out})} + \text{TIC}_{(\text{out})} + \text{CH}_4_{(\text{g})} + \text{CO}_2_{(\text{g})} + \text{Biomass(produced)} + \text{TOC (adsorbed)} \quad (4)$$

The justification for the (+) sign prior to biomass production and carbon adsorption is because the decay of biomass, especially under starved conditions, and/or the bioregeneration of the carbon surface may result in a net input of carbon into the aqueous phase. Equation 4 may be rewritten as:

$$\text{Biomass}_{(\text{produced})} + \text{TOC}_{(\text{adsorbed})} = \text{TOC}_{(\text{in})} + \text{TIC}_{(\text{in})} - \text{TOC}_{(\text{out})} - \text{TIC}_{(\text{out})} \quad (5)$$

$$- \text{CH}_4_{(\text{g})} - \text{CO}_2_{(\text{g})}$$

All the parameters on the right side of Equation 5 are measurable and may readily be incorporated into the expression. The left hand side of Equation 5, however, is not easy to evaluate directly and consequently the value of the two lumped parameters may be arrived at through the substitution of the values of the parameters on the right hand side of the equation. If the value of the quantity to the left of Equation 5 is positive, it implied that adsorption onto activated carbon and/or biomass production are occurring. On the other hand, if the left hand side of Equation 5 is negative, it implied that activated carbon bioregeneration and/or biomass decay are occurring at a faster rate than biomass production and adsorption.

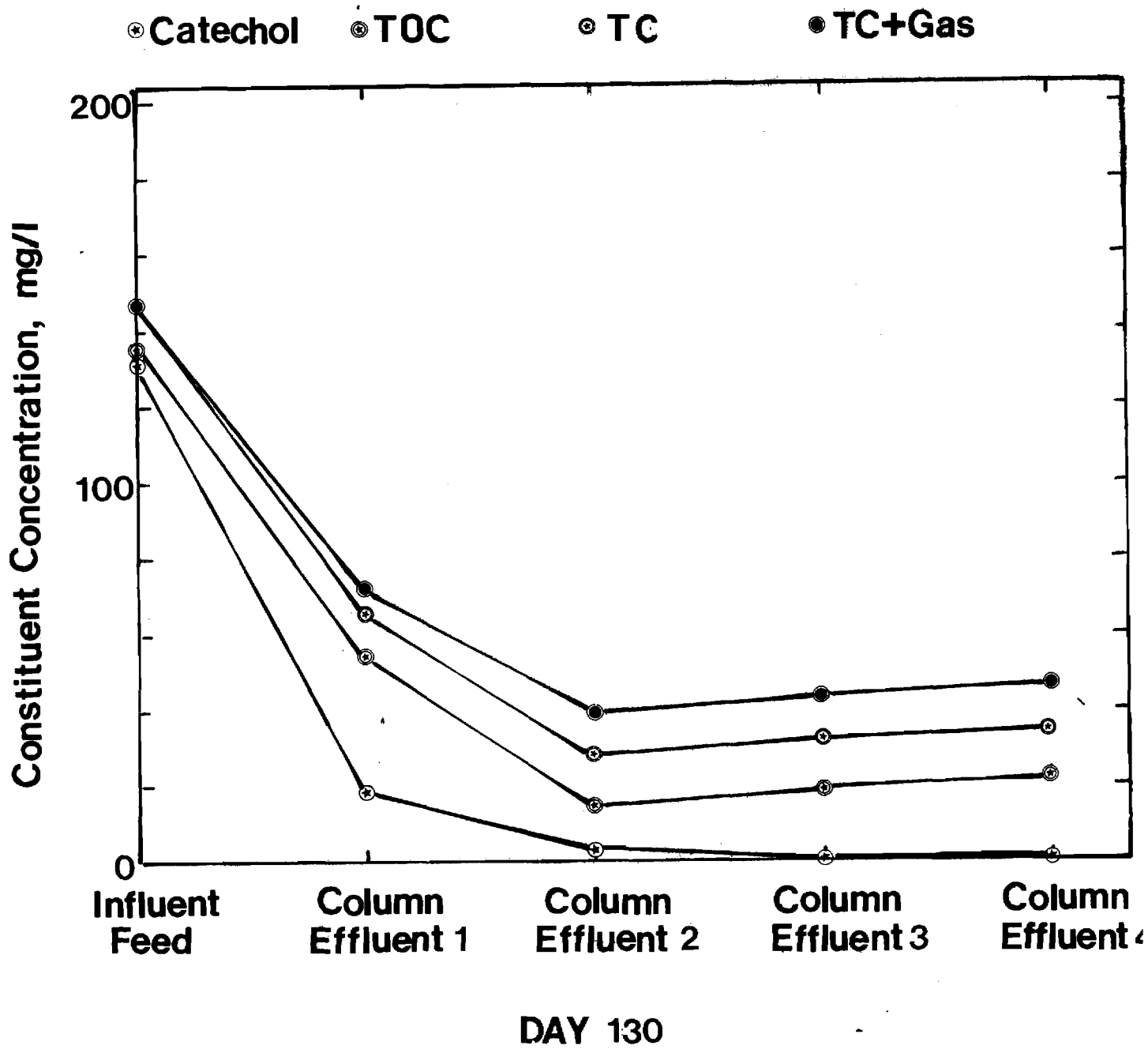
If Equation 5 is to be evaluated using concentration units in the aqueous phase, then the carbon equivalent of the carbon dioxide and methane gas produced should be converted to the aqueous phase concentration units. This is accomplished as follows:

- (a) The volume of methane and carbon dioxide, expressed in liters at STP per day is divided by the flow rate into the reactor system expressed in l/day.
- (b) The resulting quotient is then divided by the molar volume of 22.4 l and multiplied by the atomic weight of carbon, 12,000 mg to yield the carbon equivalent of the gaseous products.
- (c) The carbon equivalents of the gaseous products from the first and second column are added to the total aqueous carbon in the effluent

from the second column. This cumulative procedure is repeated for columns 3 and 4 in order to maintain the integrity of the carbon balance across the treatment system.

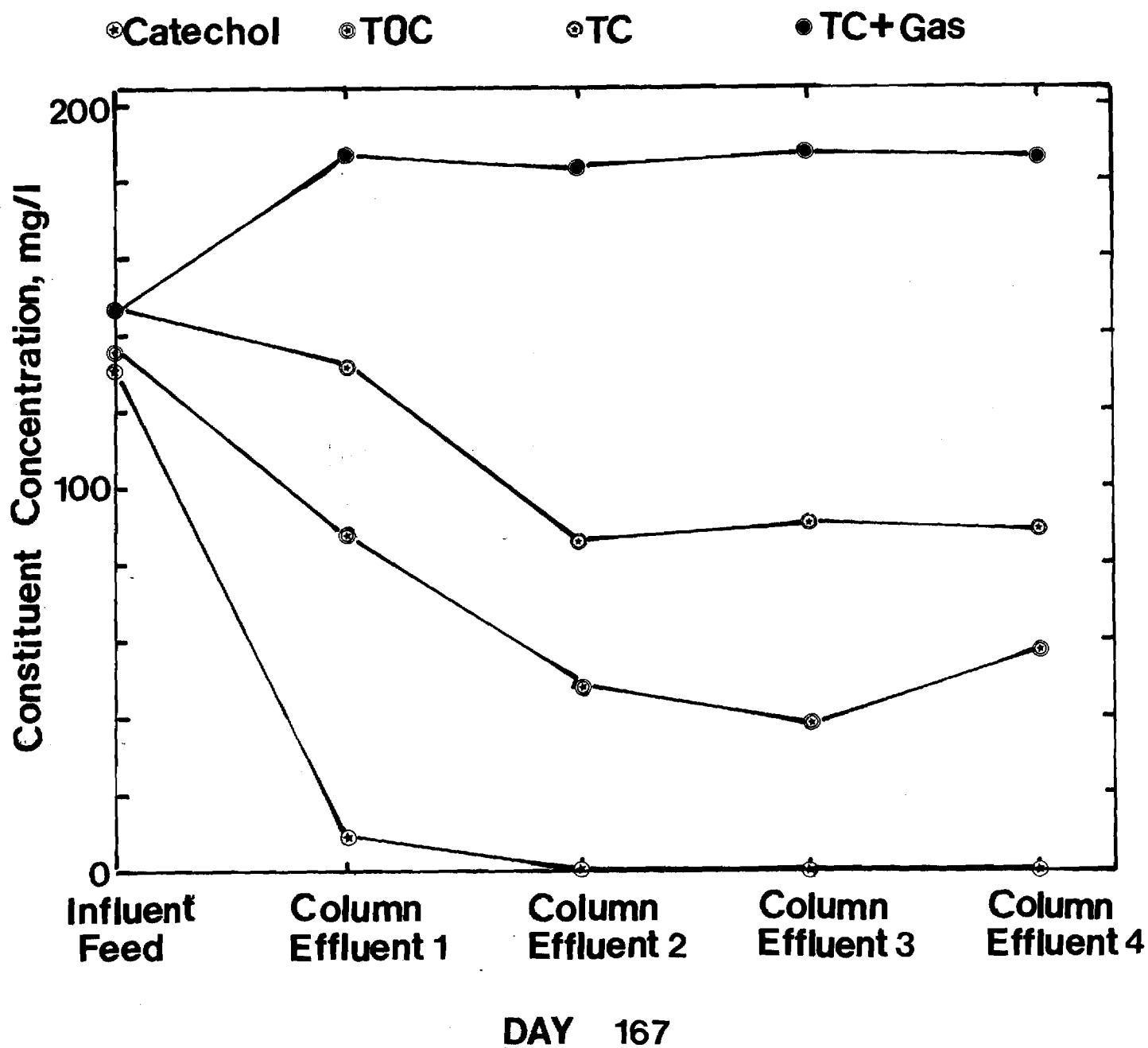
Carbon material balances across the treatment system were constructed for days 130, 167, 245 and 283 of continuous operation. The carbon material balance for day 130 (see Figure 25) represents the reactor system during the adsorption and acclimation stage of this phase of the experiment. On this day the first column was responsible for reducing the TOC in the aqueous phase by 60 percent while an additional reduction in TOC of 28.4 percent was obtained in the second column, resulting in a total reduction in TOC of 88.4 percent in the first two columns. Gas production (CH_4 plus aqueous and gaseous CO_2) from the first two columns accounts for only 11.2 percent of the organic carbon removed indicating that 88.8 percent of the TOC removed is either adsorbed onto the activated carbon or is utilized in the production of biomass. However, because of the very low biomass yield ratio reported for attached growth anaerobic systems (Young and McCarty, 1976), it is safe to assume that most of the organic carbon that was not accounted for on day 130 was adsorbed onto the activated carbon. The catechol concentration, expressed as the carbon equivalent, is also plotted in Figure 25. Catechol accounts for 97 percent of the organic carbon in the feed, however, on day 130, the catechol concentration in the effluents from the first two columns accounted for only 36.2 and 21 percent of the organic carbon content of the two column effluents. This indicates that the conversion of catechol to some other metabolic intermediates does not represent the rate limiting step in the anaerobic degradation of this phenolic compound.

The carbon material balance, shown in Figure 26, for day 167 of continuous operation represents the state of the treatment system during the accelerated



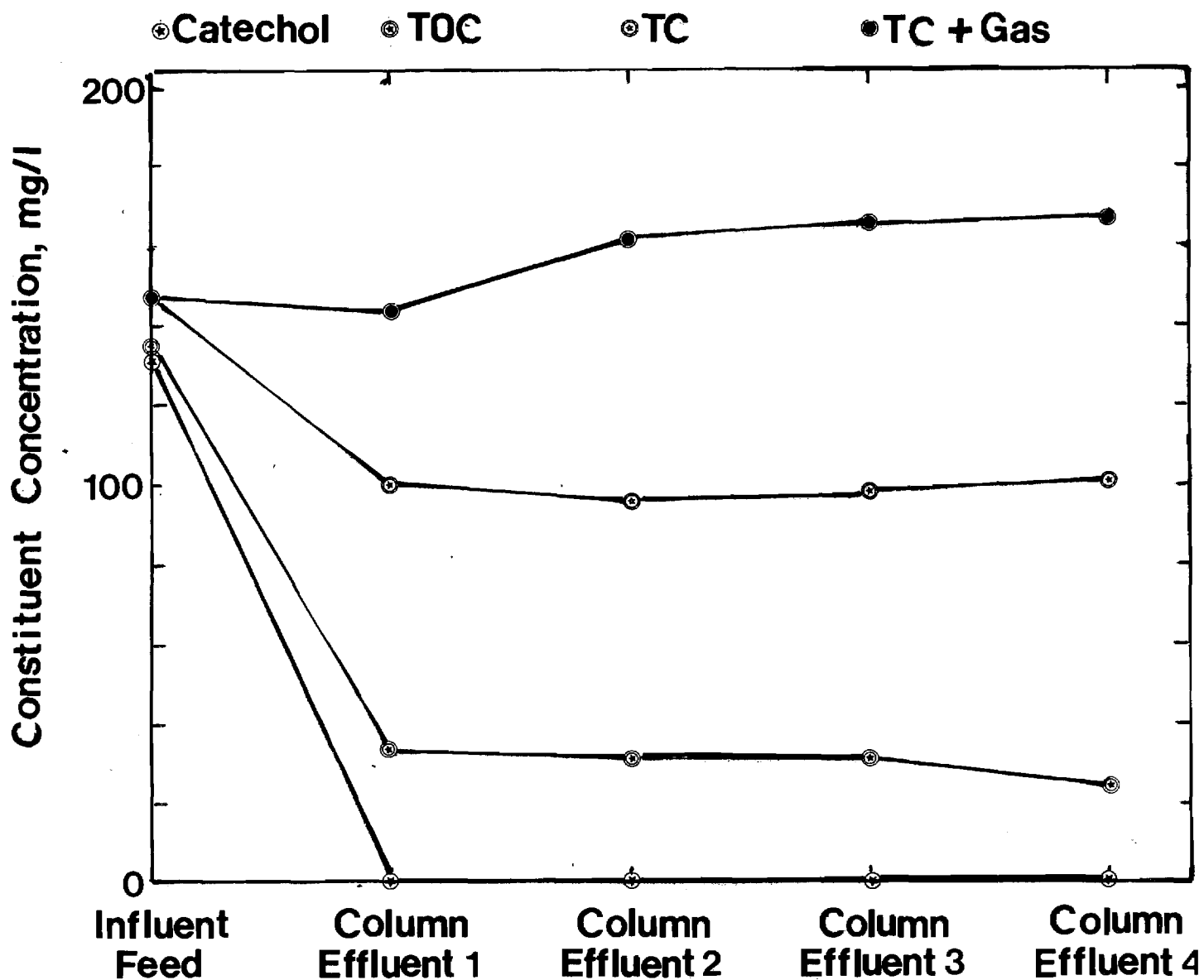
I. CARBON BALANCE ACROSS CATECHOL FED REACTOR

FIGURE 25



I. CARBON BALANCE ACROSS CATECHOL FED REACTOR

FIGURE 26



DAY 245

I. CARBON BALANCE ACROSS CATECHOL FED REACTOR

FIGURE 27

conditions, gas production from the second column was irregular and was characterized by a sequence of an organic carbon adsorption phase followed by a bioregeneration and gas production phase. The two sets of data plotted for TC + Gas in Figure 28 represent the carbon profile when the lowest steady state gas production from the second column (0) and the highest gas production rate for the same column (16.8 ml/day) are used.

At steady state 79 percent of the feed TOC is reduced in the first column while the overall reduction in TOC for the whole reactor was 84 percent.

Steady-State Performance

Steady-state intensive analysis was conducted on the feed substrate and all column effluents for the period extending from day 272 to day 283. A summary of the steady-state operating data for this phase of the experiment is presented in Table 17. These data indicate that a process consisting of one single column having an empty bed detention time of 11.62 hours is sufficient to efficiently treat the synthetic catechol wastewater and in effectively achieving reductions in: (a) TOC of 81 percent; (b) COD of 88 percent; and, (c) catechol removal exceeding 90 percent. In addition, the process was producing an 88 percent by volume methane gas. This high purity of the gaseous product is due to the relatively low organic feed strength and operating detention time as well as the high solubility of carbon dioxide in the neutral pH range.

The concentration of total and volatile suspended solids in the individual column effluents were measured during the period of intensive analysis. The concentration of suspended solids in the various column effluents fluctuated greatly because of plugging problems that were encountered during this phase of the study. This resulted in the disturbance of the columns which caused

Table 17. Average Steady-State Performance Data for
200 mg/l Catechol Fed Reactor

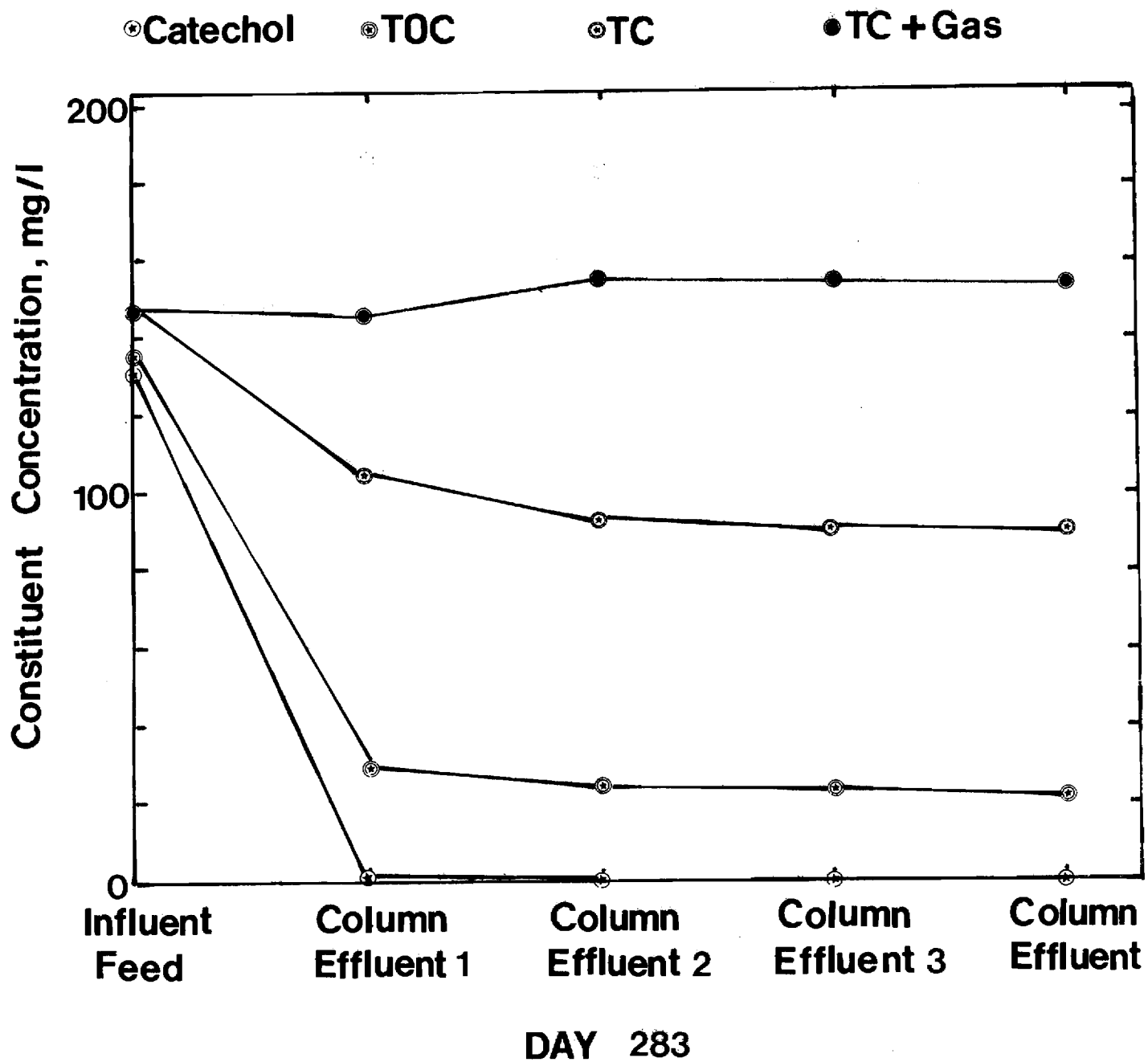
Parameter	Influent Value	Parameter Value in Column Effluents			
		1	2	3	4
pH	7.40	7.35	7.32	7.29	7.30
TOC, mg/l	134	26	26	23	26
TIC, mg/l	5	63	68	71	63
COD, mg/l	420	50	30	30	20
Catechol, mg/l	200	2.1	1.2	1.3	1.2
Gas Production, ml/day		288	16	0	0
Methane, ml/day		254	15	0	0
Carbon Dioxide, ml/day		6	1	0	0
Nitrogen, ml/day		28	0	0	0
Alkalinity, mg/l as CaCO ₃	1920	2256	2088	2058	2082
NH ₃ -N, mg/l	26.8	11.0	9.7	1.3	6
TKN, mg/l	-	10.5	-	11.7	13.4
ORP		-492	-416	-197	-

exceedingly high effluent suspended solids to be encountered. During the normal operation of the process, however, the suspended solids concentration in the column effluent were much lower. The data in Figure 29 represent the total and volatile suspended solids measured in the column effluents during this period of operation. The volatile suspended solids averaged around 58 percent of the total suspended solids.

Alkalinity data varied very little across the reactors during the period of intensive analysis, ranging from 1884-2256 mg/l as CaCO_3 . The titration curves shown in Figures 30, 31, 32 and 33 show that the treatment process did not cause a depletion in the buffer capacity of the system which is usually taken as a sign of complete degradation of the organics present in the feed and the absence of the intermediate volatile fatty acids in the column effluents.

Hydrogen utilization and methane formation experiments were conducted in triplicate on all effluent samples as well as on granular activated carbon samples withdrawn from all reactors. The gas composition in the head space of every vial, after an 84 hour incubation period at 37°C , is given in Tables 18 and 19. The data in Tables 18 and 19 clearly indicate that the methanogenic activity is much more intense in the first column medium and aqueous phase than it is in the remaining three columns. This observation agrees strongly with the fact that the first column is responsible for almost all of the methane produced by the reactor system.

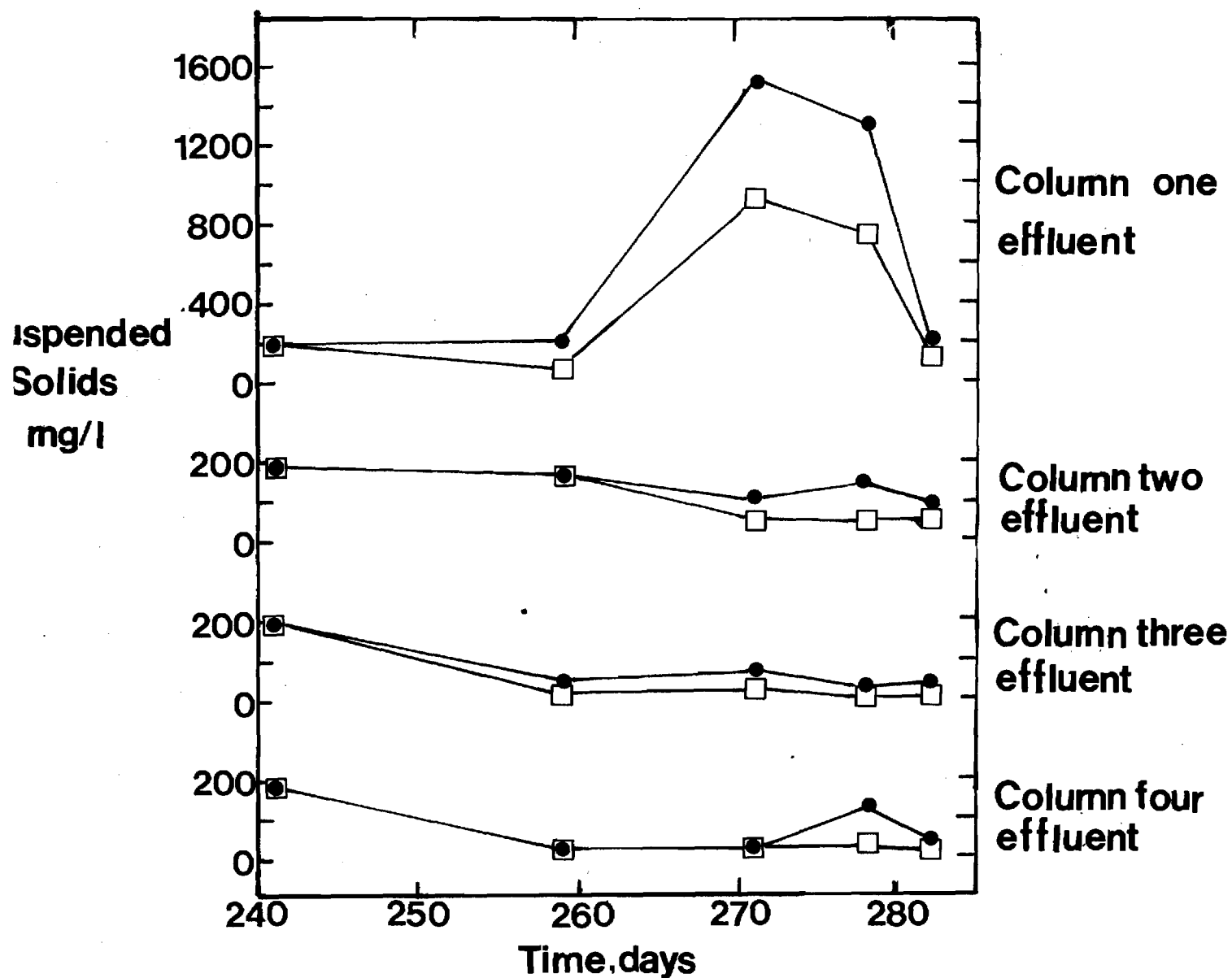
Care must be taken in comparing the data presented in Table 18 with that in Table 19. A higher head space methane composition was always observed in the head space of the samples inoculated with aqueous samples than was observed from the vials inoculated with activated carbon granules. This discrepancy in the results is due to the relatively large aqueous inoculum



I. CARBON BALANCE ACROSS CATECHOL FED REACTOR

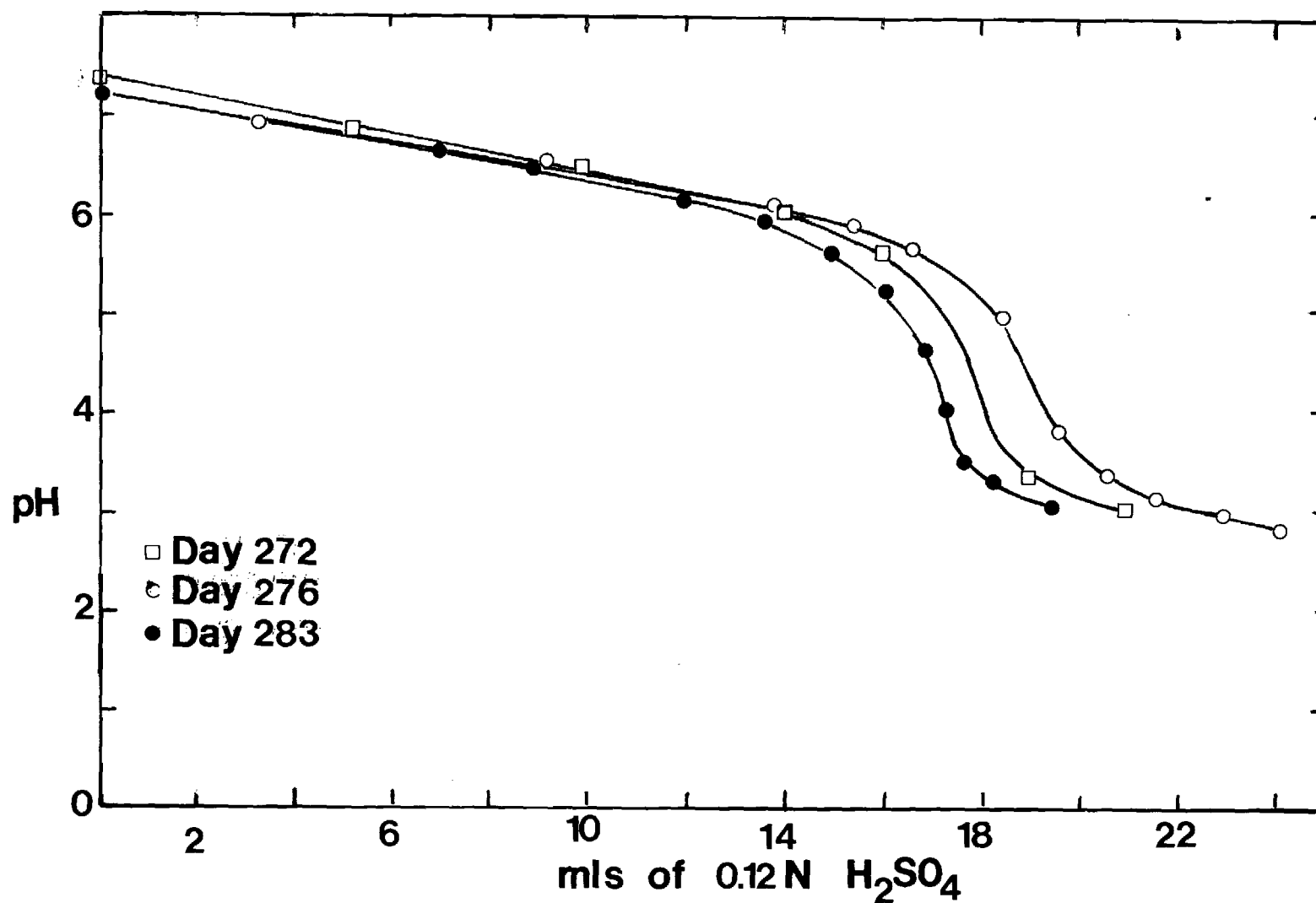
FIGURE 28

- Total Suspended Solids
- Volatile Suspended Solids

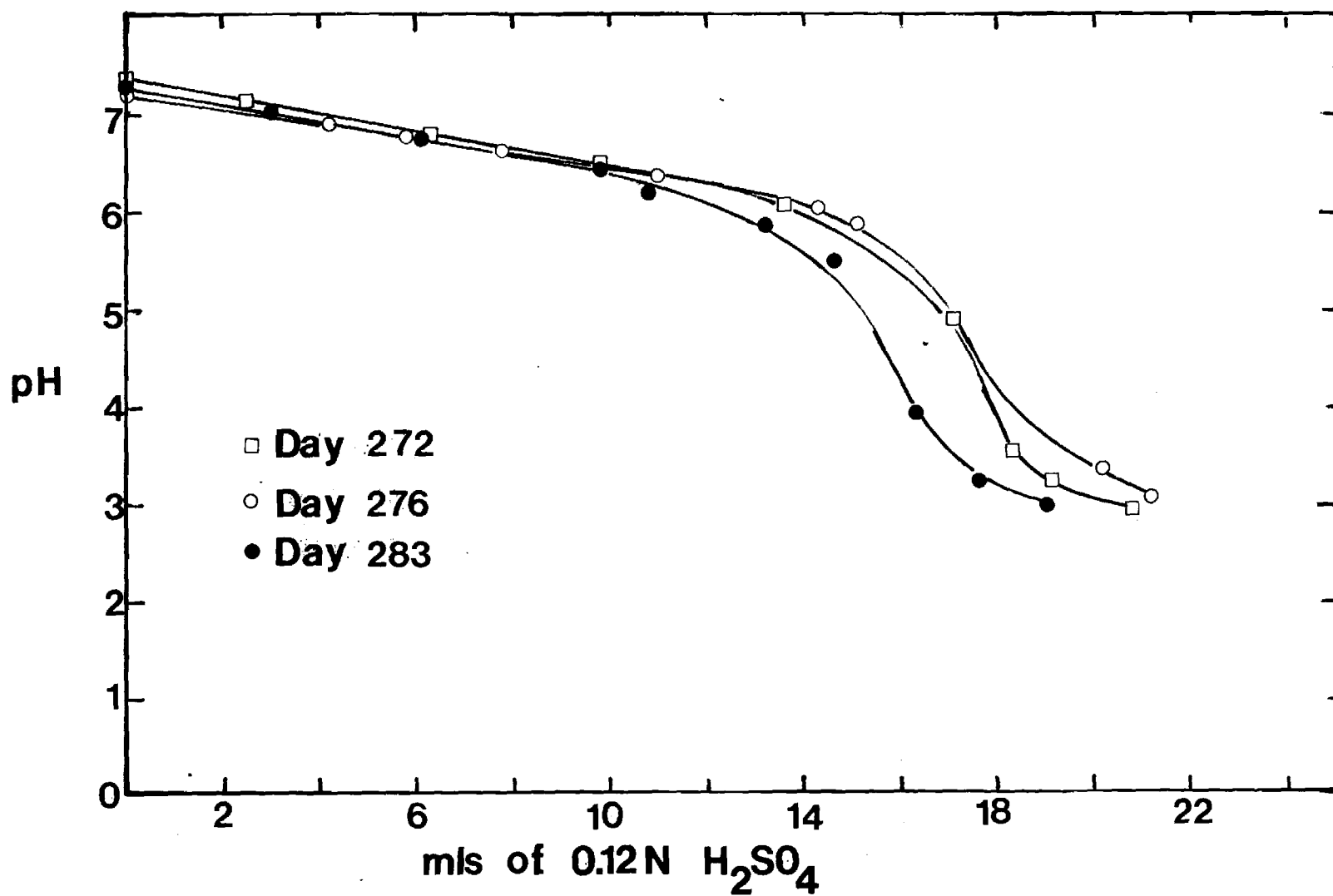


SUSPENDED SOLIDS CONCENTRATION OF INDIVIDUAL COLUMNS FROM CATECHOL FED REACTOR

FIGURE 29

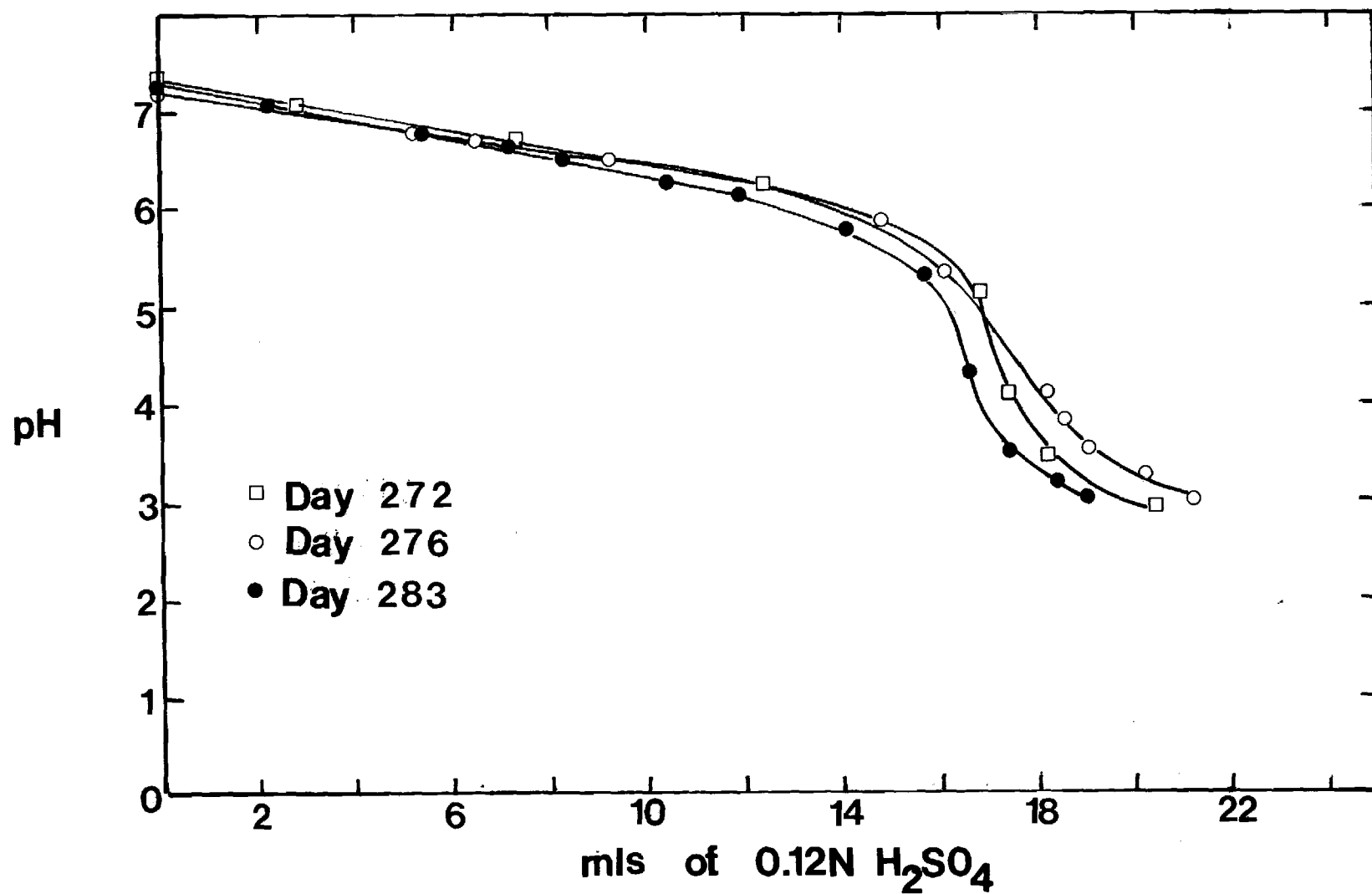


I. BUFFERING CAPACITY OF CATECHOL COLUMN ONE
FIGURE 30

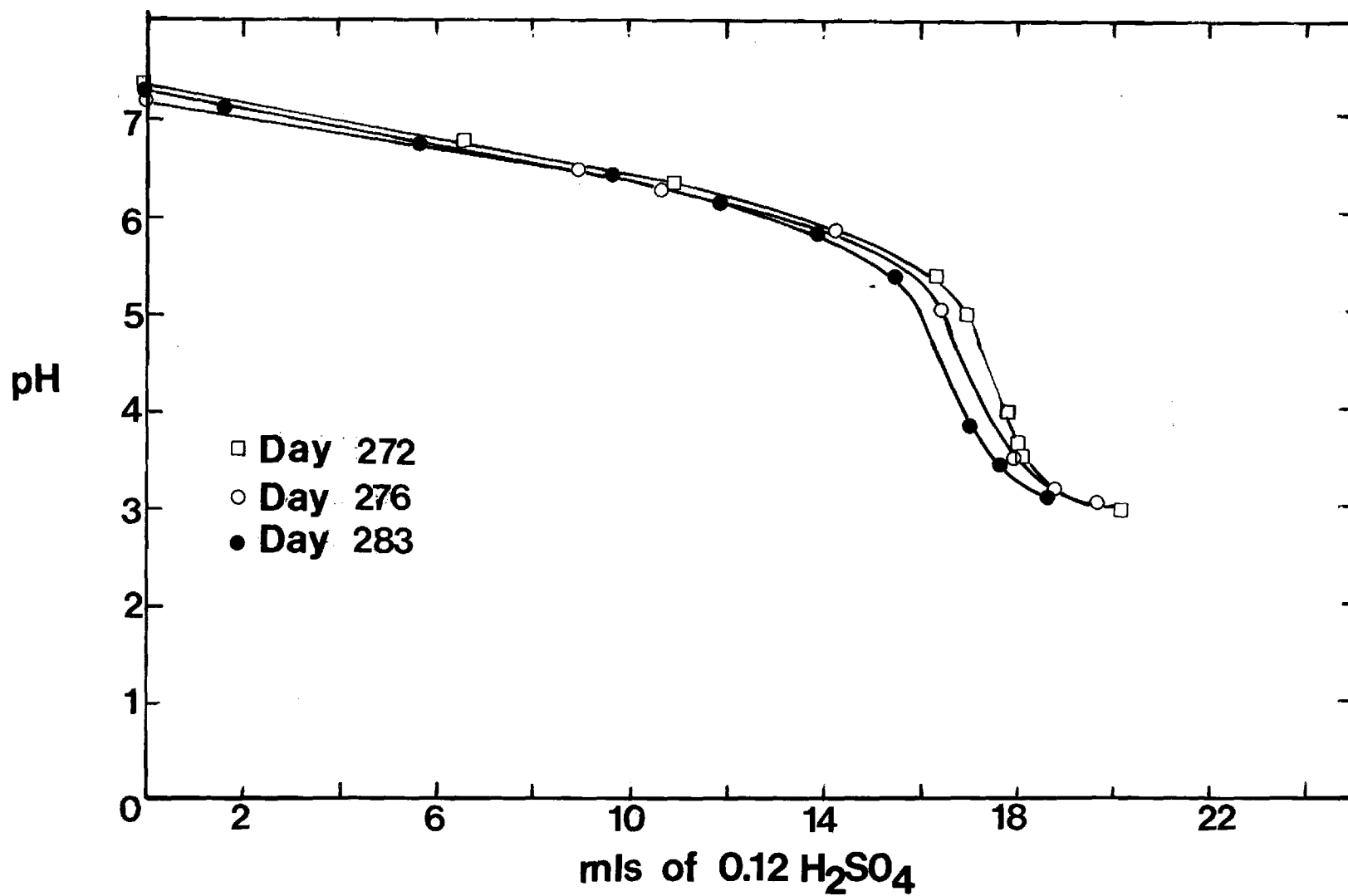


I. BUFFERING CAPACITY OF CATECHOL COLUMN TWO

FIGURE 31



I. BUFFERING CAPACITY OF CATECHOL COLUMN THREE
FIGURE 32



I. BUFFERING CAPACITY CATECHOL COLUMN FOUR
FIGURE 33

Table 18. Hydrogen Utilization and Methanogenesis Tests on
Effluent Samples from 200 mg/l Catechol Fed Reactor

Effluent from Column	Percent Gas Composition		
	Methane	Carbon Dioxide	Hydrogen
1	74.73	2.84	14.65
1	63.23	1.29	9.09
1	47.90	3.10	4.04
2	13.41	1.03	79.68
2	11.11	1.29	83.42
2	7.28	1.55	34.42
3	9.96	1.16	83.42
3	9.96	1.86	77.64
3	13.80	1.29	75.38
4	9.77	1.6	80.40
4	9.58	1.86	83.92
4	7.36	1.81	86.93

Table 19. Hydrogen Utilization and Methanogenesis Tests
on the Activated Carbon Medium

Activated Carbon from Column	Percent Gas Composition		
	Methane	Carbon Dioxide	Hydrogen
1	2.30	0.26	94.22
1	0.77	0.13	98.99
1	3.45	0.26	95.48
2	1.92	0.39	94.47
2	1.92	0.39	94.47
2	1.42	0.39	93.62
3	4.22	0.00	91.67
3	1.15	0.34	94.97
3	0.96	1.29	93.97
4	1.42	0.26	98.99
4	0.96	1.29	95.45
4	1.15	1.26	97.47

volume (7 ml) used in the effluent inoculated vials versus the few carbon granules used in the activated carbon inoculated vials.

To further emphasize the importance of the activated carbon as an attachment surface, electronmicroscopic pictures of the carbon surface (see Figures 34 and 35) reveal the presence of a thick slime layer covering the carbon granule.

Phase II, 400 mg/l Catechol

During this phase of the catechol degradation experiment, the catechol concentration in the synthetic feed substrate was increased to 400 mg/l while keeping the feed flow rate and the recirculation flow rate at the same levels used in the first phase of the experiment, namely 2 ml/min and 50 ml/min, respectively. The synthetic feed substrate was prepared daily in four liter batches using 28 ml of the salt solution, 80 ml of the phosphate buffer solution, 1.6 g of catechol and distilled water. The theoretical COD and TOC concentration of the feed substrate computed using the measured values for the salt solution and the theoretical values for catechol given in Table 15 were 936 and 308 mg/l, respectively. The measured values of the two parameters COD and TOC in the feed as obtained from the average of 19 duplicate readings were 940 and 255 mg/l, respectively. These computations and measurements yield a computed COD to TOC ratio of 3.04 and a measured ratio of 3.69.

The feed substrate was maintained at a pH of 7.4 throughout this phase of the experiment. A titration curve on the feed substrate (see Figure 14) indicates this feed to have a buffer capacity almost identical to the substrate utilized in phase 1. This similarity is due to the fact that the two substrates have very similar phosphate contents and that because catechol has a pK_a of 10.0 at 20°C it will not contribute to the buffer capacity in the pH

Electron Micrograph of Carbon Surface

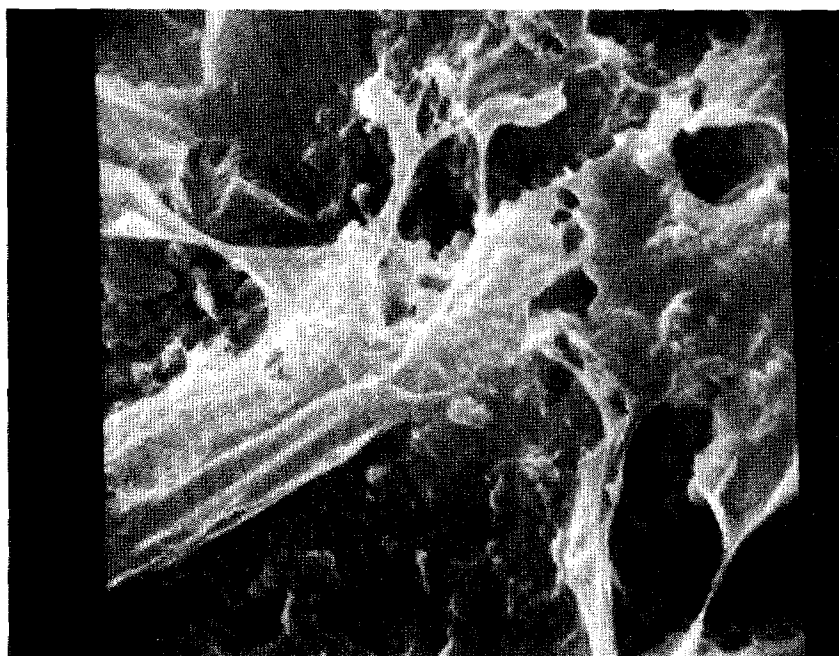


Figure 34

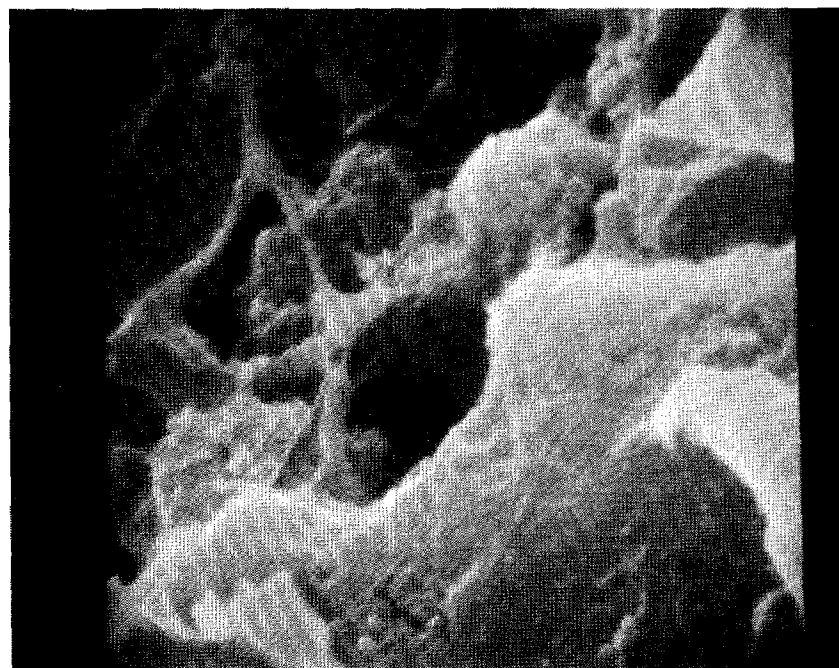
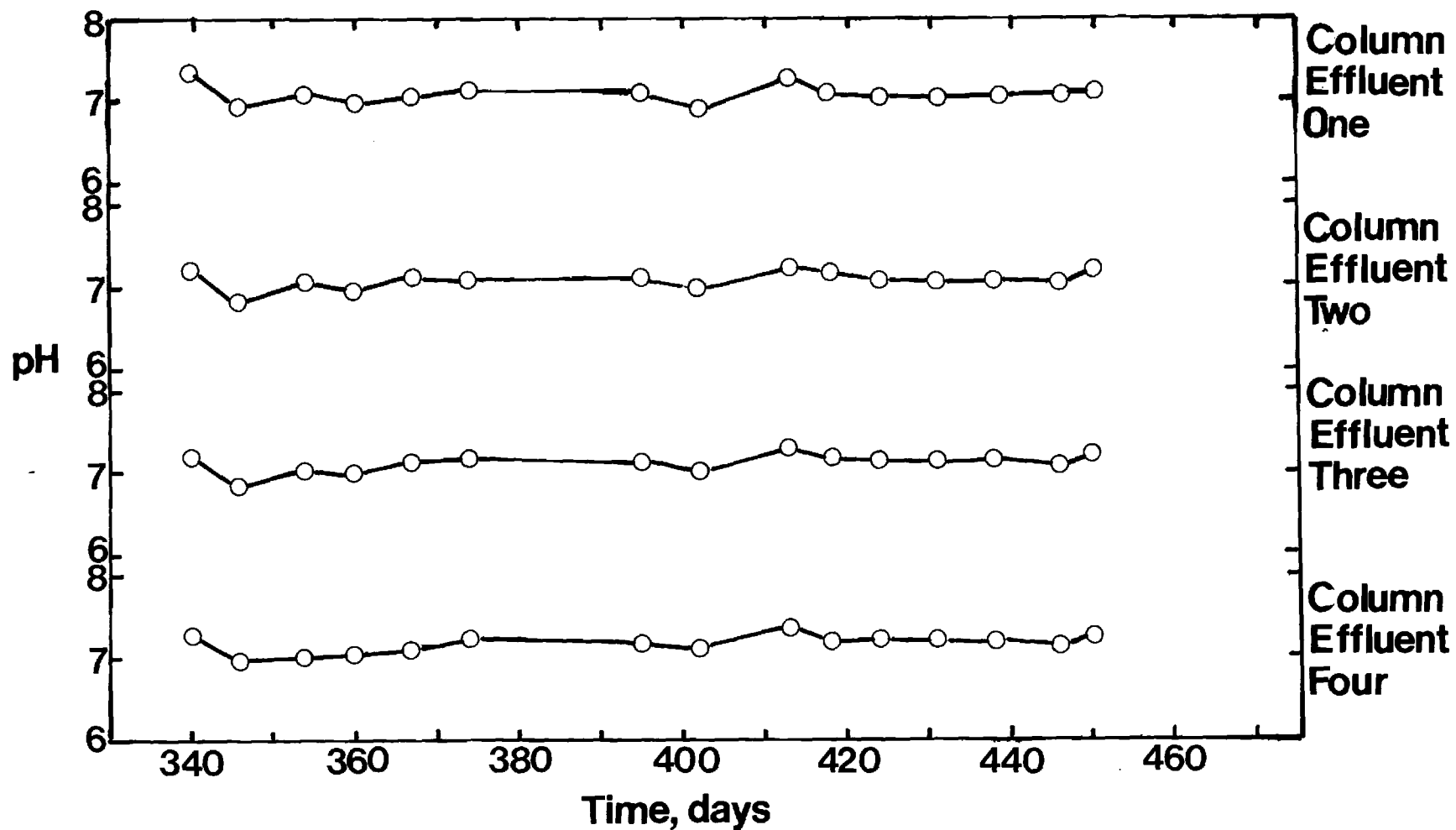


Figure 35

range of 7.4 to 2.5. The pH in the effluents from the four columns ranged from 6.83 to 7.39. The ranges of pH observed in the individual column effluents were 6.92 to 7.39 for column 1; 6.83 to 7.24 from column 2; 6.85 to 7.28 from column 3; and 6.97 to 7.39 from column 4. The average pH values observed in the four column effluents during this phase of the study were 7.09, 7.10, 7.13 and 7.19 (see Figure 36).

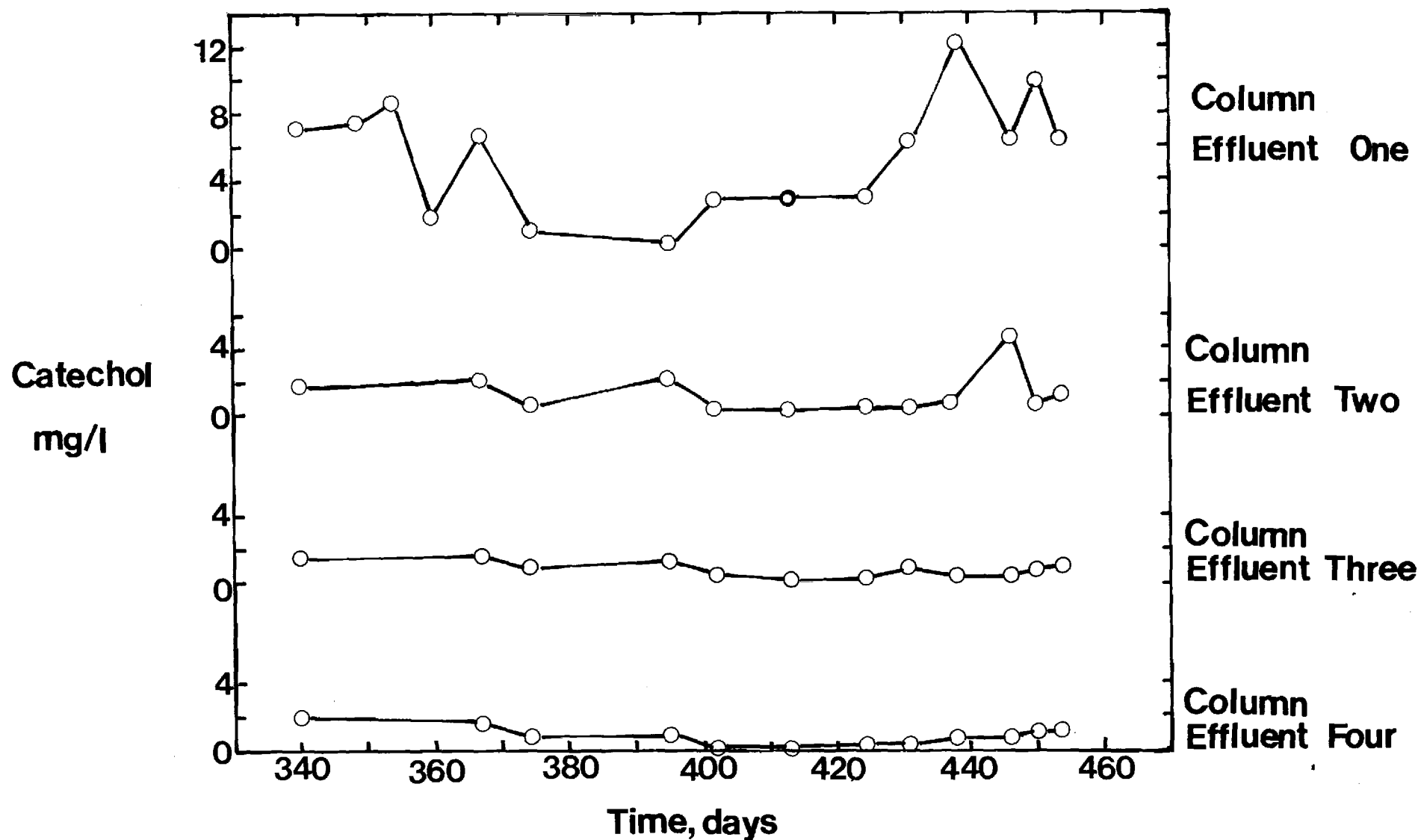
The general response of the first column to an increase in the feed concentration of catechol was an immediate increase in the rate of gas production indicating that no additional acclimation period was needed and no shock effects were encountered. Steady state conditions were attained relatively fast when compared with the period of operation needed for the attainment of steady state in the first phase of the project.

Catechol Reduction. The concentration of catechol measured in the individual column effluents is presented in Figure 37 for the period extending between day 340 and 457 of continuous operation. Once more, absorbance at 268 nm was used as a measure of catechol concentration and, consequently, all the catechol concentration values reported in Figure 37 represent upper limits on the actual catechol concentration while a lower limit may very well be zero. The measured catechol concentrations ranged from a high of 12 mg/l to a low of 0.2 mg/l in the effluent from the first column resulting in a catechol removal efficiency consistently better than 97 percent. The highest catechol concentration encountered in the effluent from the second column was 4.5 mg/l while the lowest value measured from the same column was 0.1 mg/l. Effluent catechol concentrations from the last two columns were consistently less than 2 mg/l. Average effluent catechol concentrations measured in the four column effluents during the steady-state period extending from day 458 to day 511 were 3.42,



II. pH OF INDIVIDUAL COLUMN EFFLUENTS FROM CATECHOL FED REACTOR

FIGURE 36



II. CATECHOL CONCENTRATION OF INDIVIDUAL COLUMN EFFLUENTS FROM CATECHOL FED REACTOR

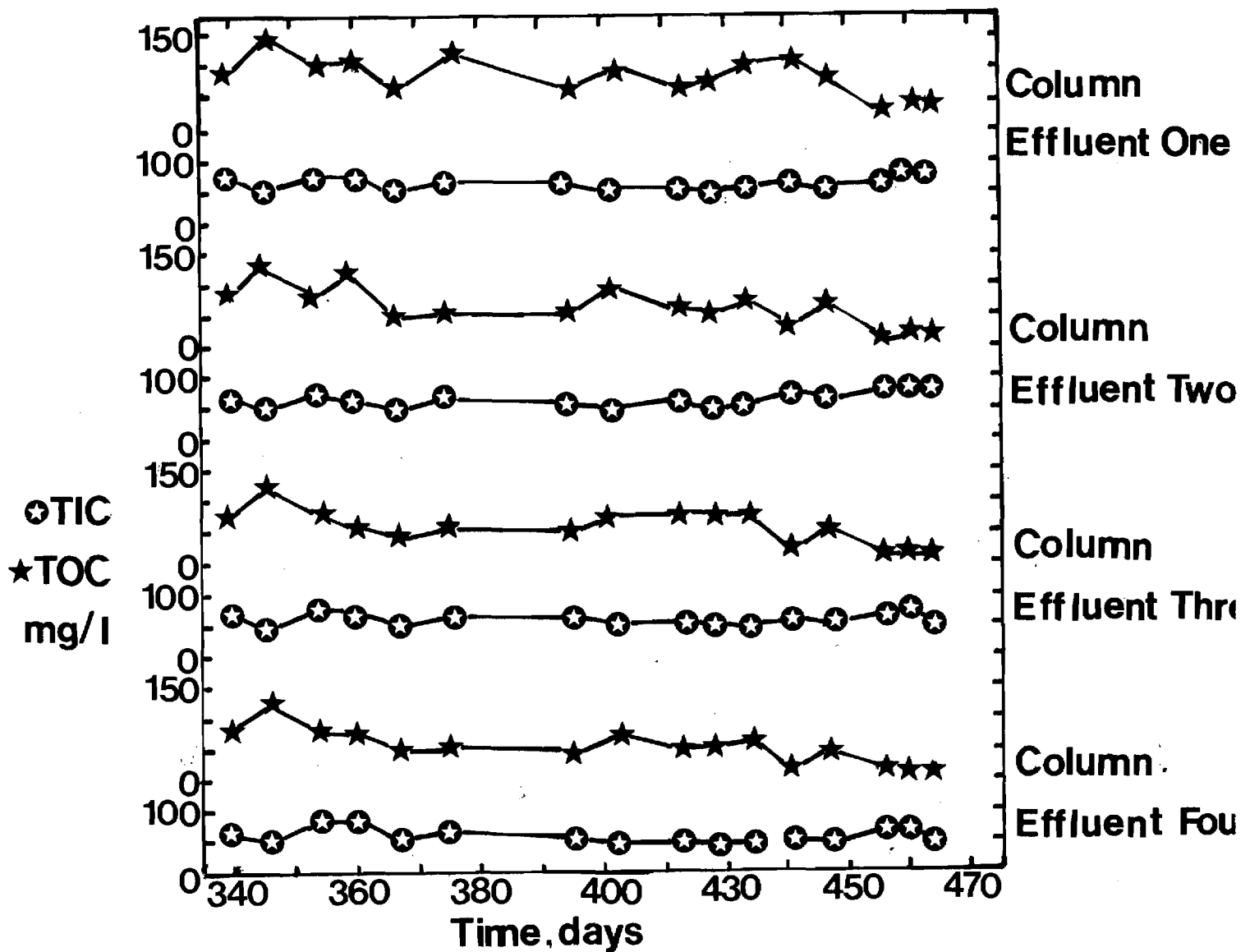
FIGURE 37

1.43, 1.34 and 0.88 mg/l, respectively. These values correspond to catechol removal efficiencies exceeding 99.15, 99.64, 99.67 and 99.78 percent.

Organic and Inorganic Carbon. The organic and inorganic carbon content of the effluents from all four anaerobic filter columns is presented in Figure 38 for the period extending from day 340 to day 464 of continuous operation. The average TOC in the feed was 255 mg/l while the organic carbon content of the effluent from the first column decreased from an average of 120 mg/l during the first 25 days of operation down to an average value of 40 mg/l near the end of this phase of the experiment. The organic carbon content of the effluents from the last three columns average around 34, 32 and 25 mg/l when steady state operating conditions were attained. These steady-state effluent TOC concentrations correspond to removal efficiencies of 84.3, 86.7, 87.4 and 90.2 percent in the respective four columns.

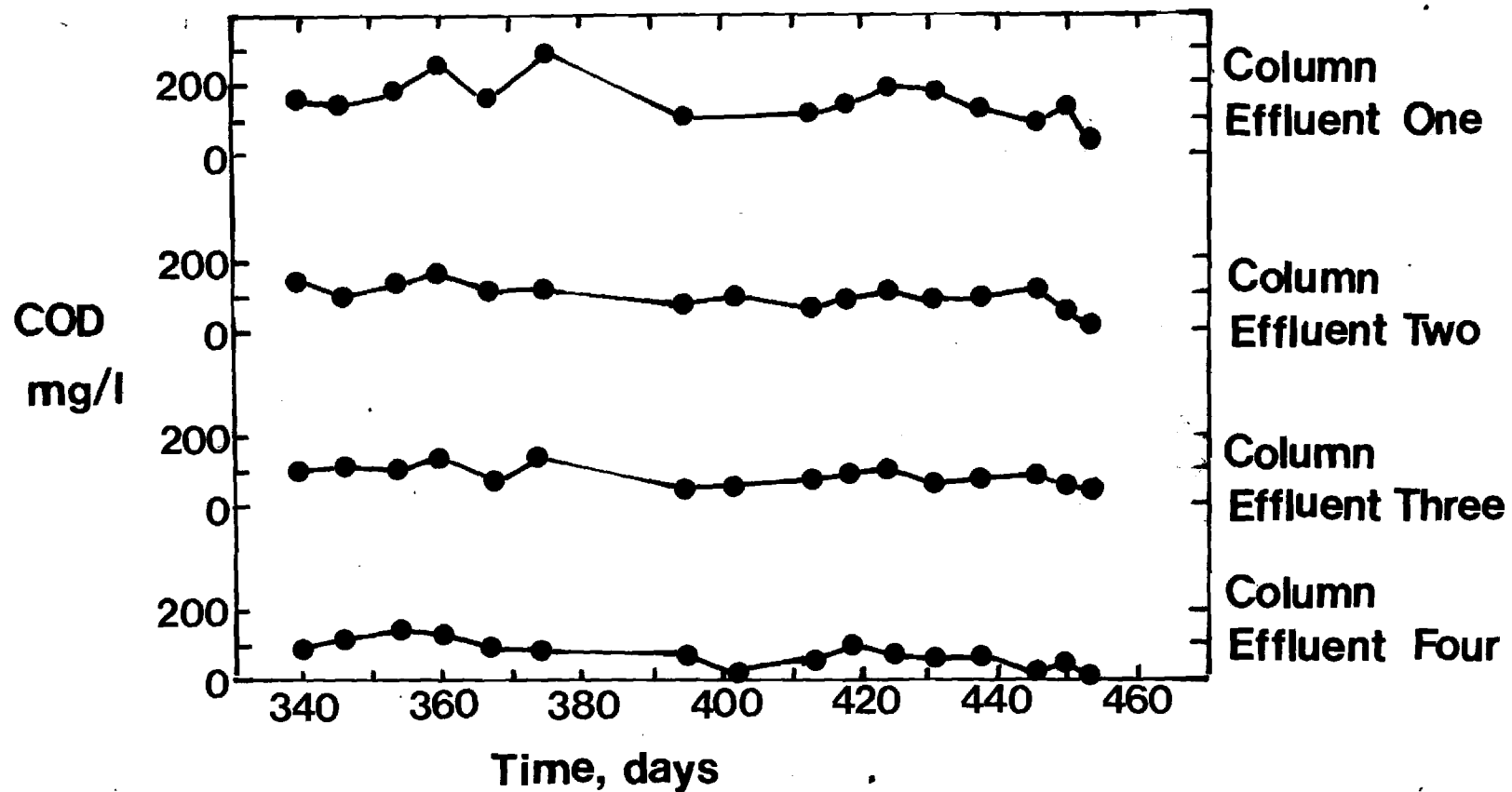
Chemical Oxygen Demand. The chemical oxygen demand of the individual column effluents for the period extending from day 340 to day 464 is shown in Figure 39. The initial COD measurements for the effluents from columns 1 through 4 were 167, 146, 102 and 98 mg/l whereas final steady-state COD values found in the four column effluents averaged around 65, 54, 51 and 55 mg/l, respectively. These steady-state COD effluent concentrations correspond to removal efficiencies of 93, 94, 94.6 and 94 percent from the four respective columns. Once again, the first column was responsible for practically all the COD removal accomplished in the treatment process.

Gas Production. The cumulative total dry gas produced from the individual columns that registered gas production during this phase of the experiment (columns one and two), and the total cumulative gas produced by the experimental reactor are presented in Figures 40, 41 and 42. During the first 30 days of



II. TIC AND TOC CONCENTRATIONS OF INDIVIDUAL COLUMN EFFLUENTS FROM CATECHOL FED REACTOR

FIGURE 38



II. COD CONCENTRATION OF INDIVIDUAL COLUMN EFFLUENTS FROM CATECHOL FED REACTOR

FIGURE 39

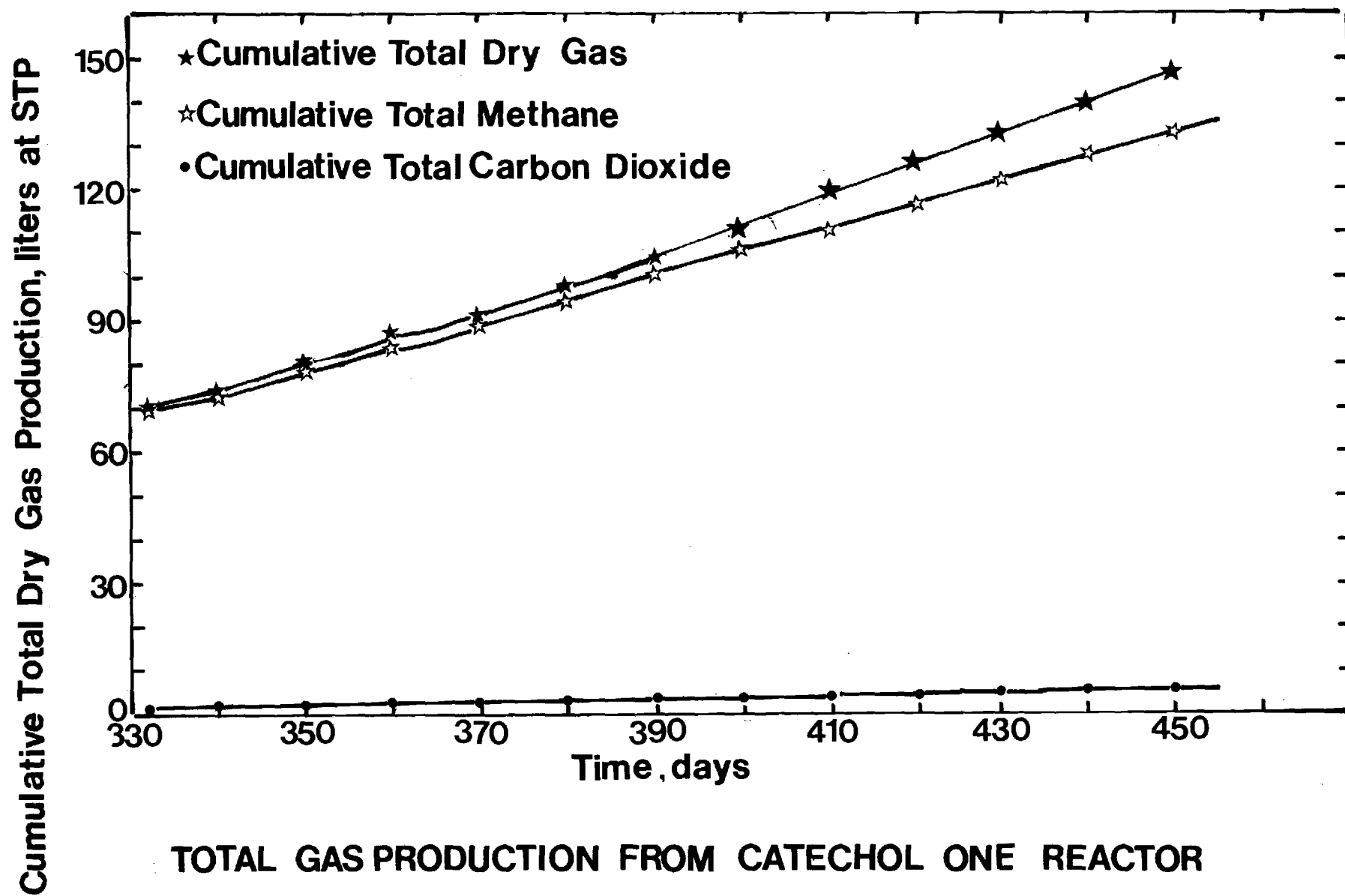
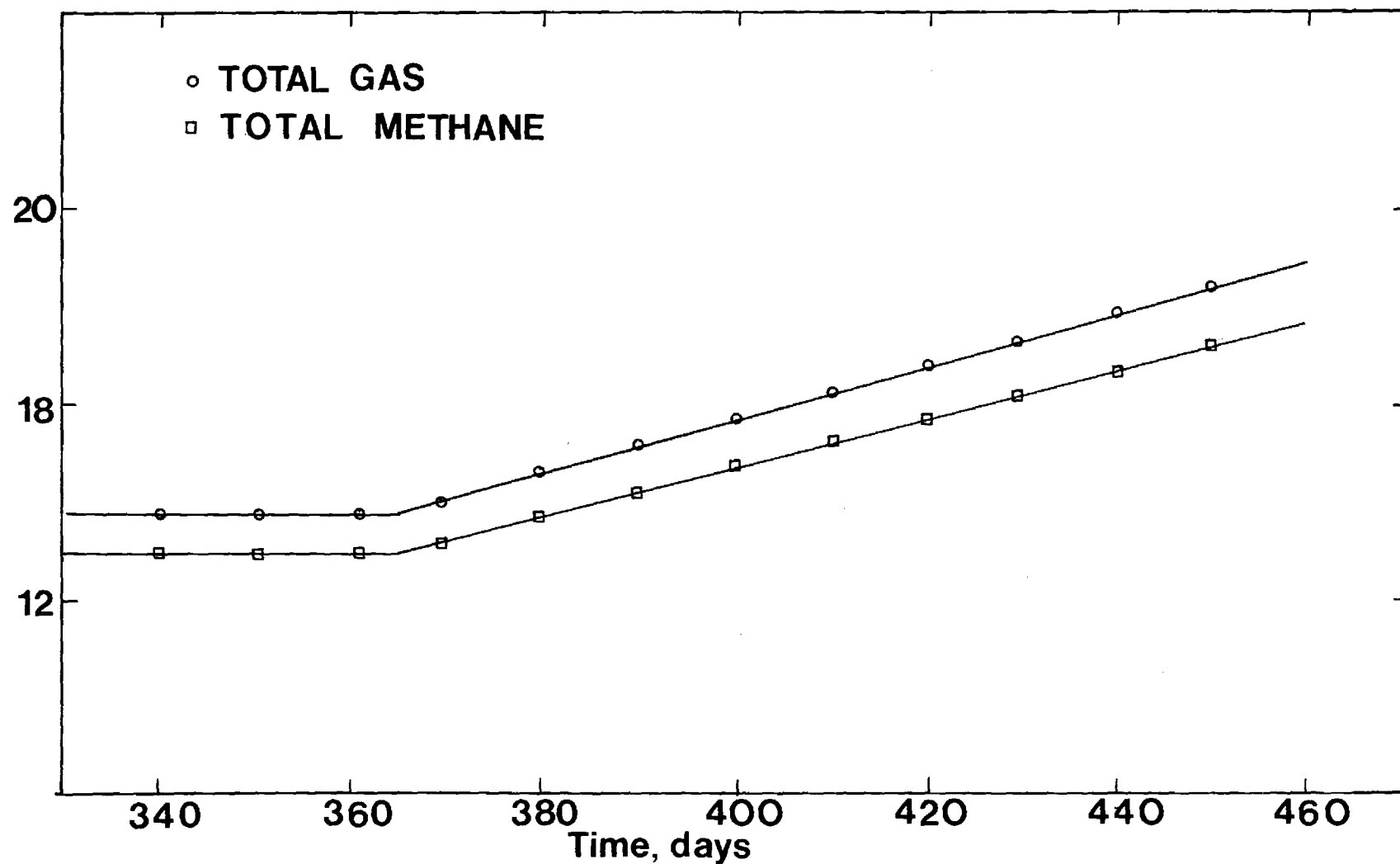


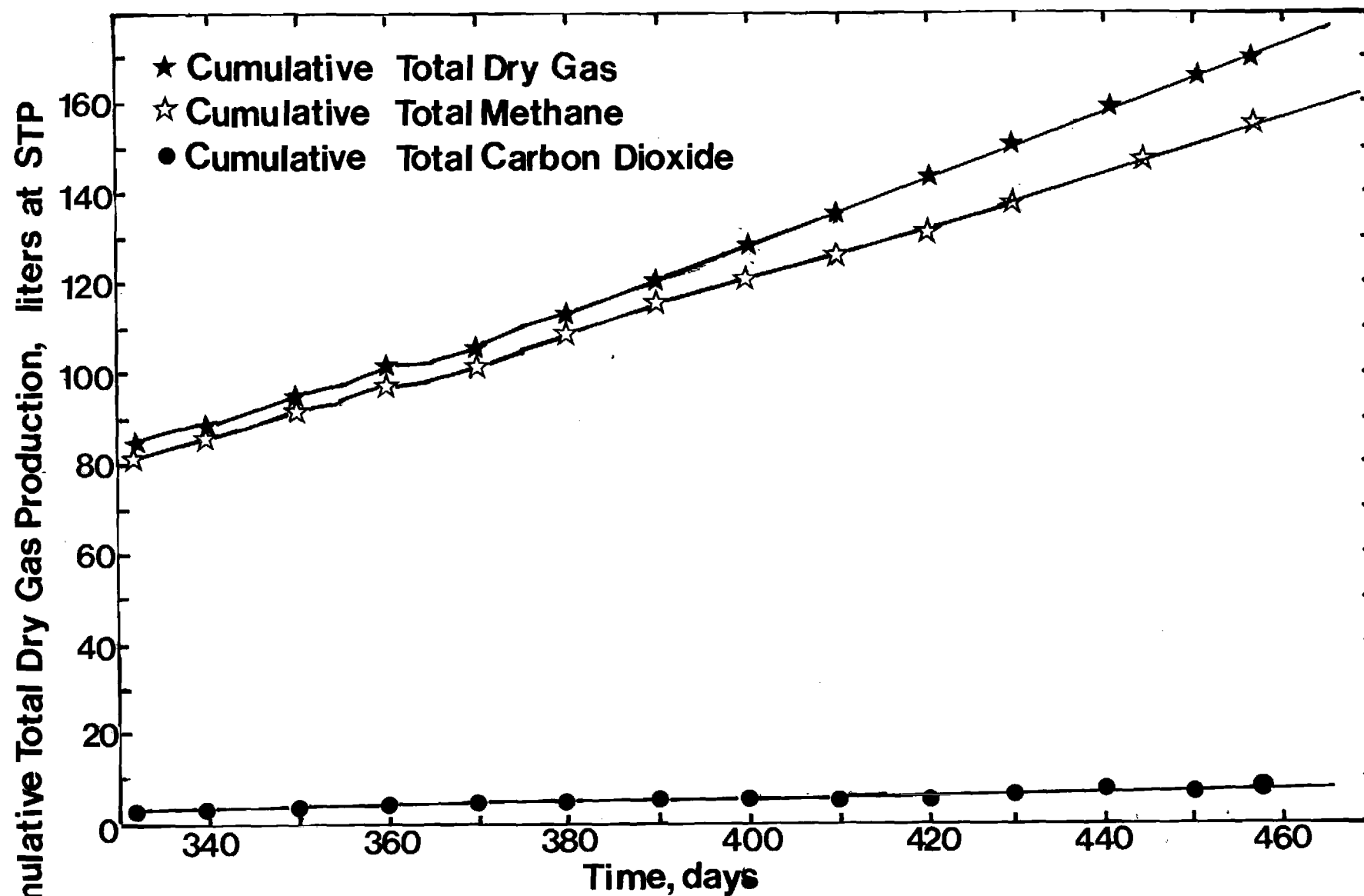
FIGURE 40

CUMULATIVE TOTAL DRY GAS PRODUCTION, liters at STP



TOTAL GAS PRODUCTION FROM CATECHOL TWO REACTOR

FIGURE 41



II. TOTAL GAS PRODUCTION FROM CATECHOL FED REACTOR

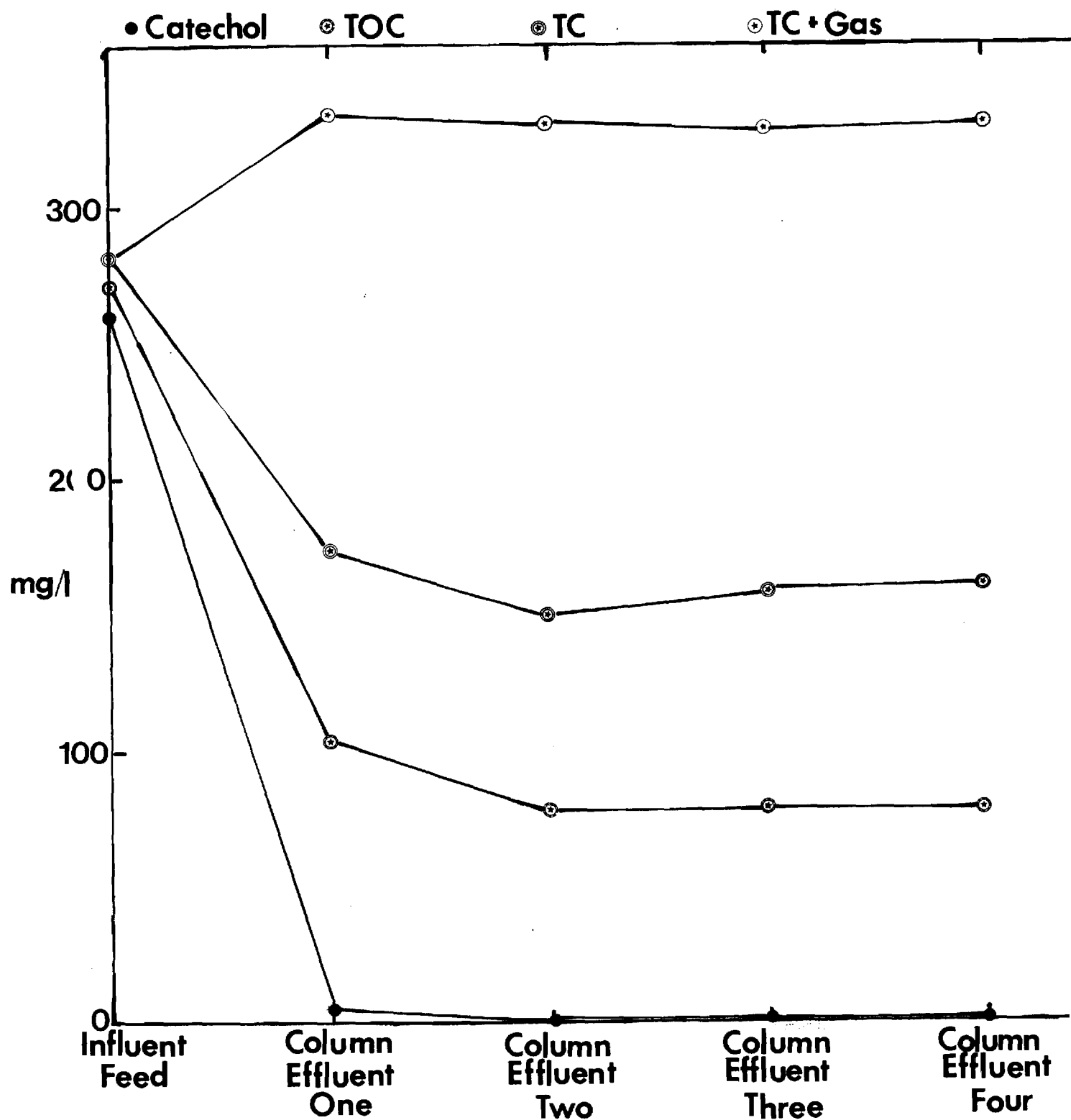
FIGURE 42

this phase of the study, gas production from the first column averaged around 629.7 ml/day of methane and carbon dioxide. During this same period gas production was observed from the second column indicating that biological activity was restricted at this stage of the experiment to the first reactor. The TOC content of the effluent from the first column averaged around a 100 mg/l during this period indicating that the second column was no longer operating under starved conditions as it did during the first phase of the experiment. However, no appreciable gas production was evident from the second column.

A carbon material balance across the experimental system taken on day 354 of continuous operation (20 days into this phase of the experiment) indicates an increase in the total aqueous and gaseous carbon content of the effluent of the system over the feed carbon content (see Figure 43). This signifies that the first column of the reactor system is undergoing active bioregeneration suggesting that increased feed catechol concentration may have led to a stimulation in the biological activity of the first anaerobic filter.

After day 365 of continuous operation, the second anaerobic filter column started exhibiting anaerobic activity in the form of gas production at a steady rate of 136 ml/day throughout the duration of this phase of the experiment. The gas production rate from the first column continued at a uniform rate of 629.7 ml/day until around day 390 when it increased to a steady state level of 735 ml/day.

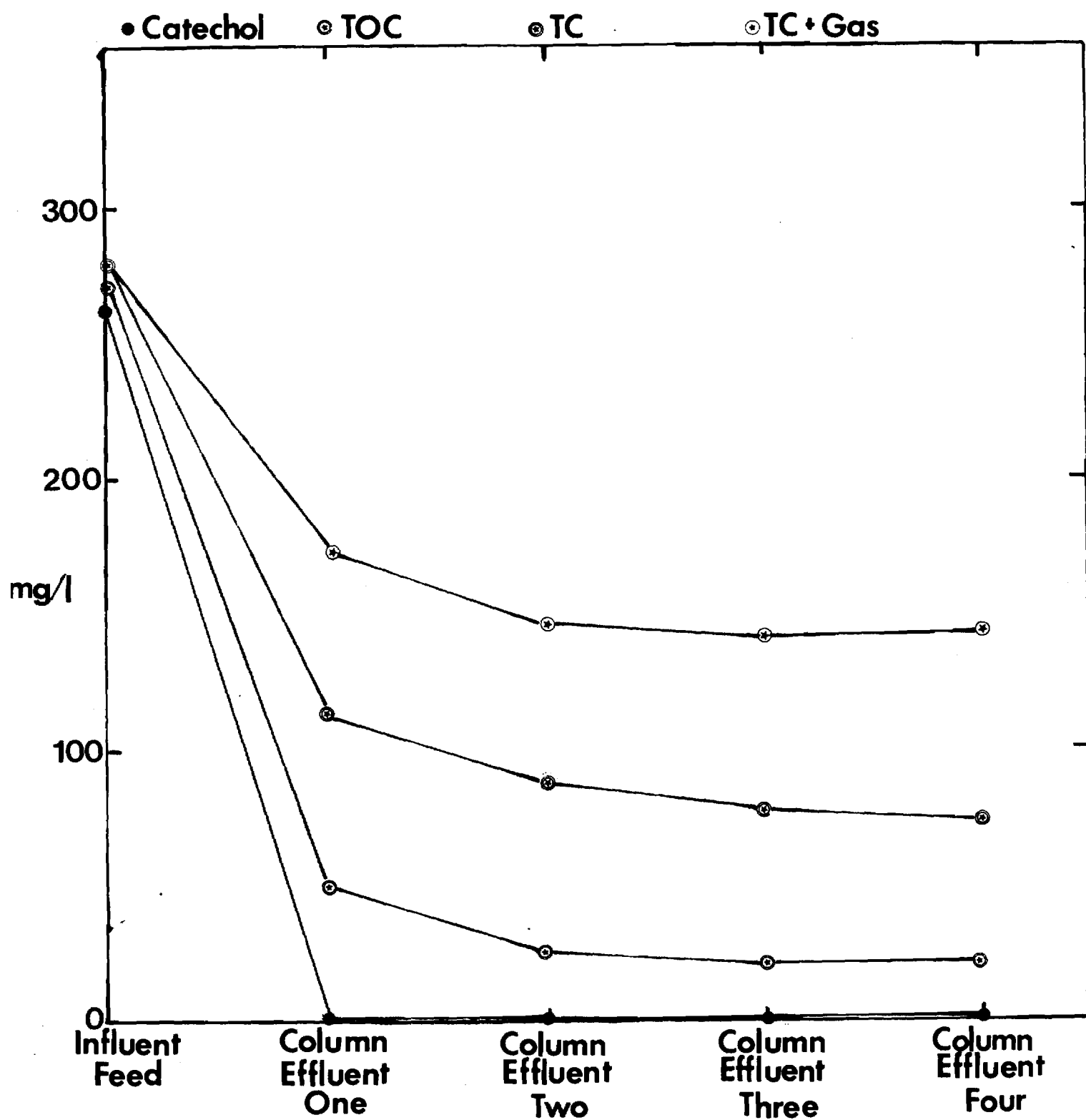
A material balance across the experimental reactor during steady-state operation indicates that the biological activity within the treatment system is limited to the first two columns (see Figure 44). At steady state, 14.3 percent of the total carbon in the feed substrate was not accounted for.



Day 354

II. CARBON BALANCE ACROSS CATECHOL FED REACTOR

FIGURE 43



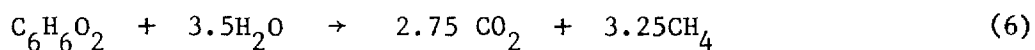
Day 457

II. CARBON BALANCE ACROSS CATECHOL FED REACTOR

FIGURE 44

This unaccounted for carbon may either be utilized in the production of biomass or it may be attributed to the partial loss of inorganic carbon from the samples upon exposure to the atmosphere and prior to analysis for TIC.

Healy et al. (1977) demonstrated using the Buswell Equation that the anaerobic degradation of catechol results in a 54.17 percent methane rich product while the remaining carbon is converted to gaseous and aqueous carbon dioxide.



The gaseous product obtained during the steady-state operation of the treatment system contained an average of 70 ml/day carbon dioxide and 801 ml/day of methane. The concentration carbon equivalent of the gas product translates to 13 mg/l carbon dioxide and 149 mg/l of methane. An additional 64 mg/l of the carbon dioxide produced is present in the aqueous phase as TIC resulting in a total inorganic carbon production of 77 mg/l. Using the theoretical composition of the anaerobic degradation products and assuming that the measured value for the methane production rate is correct, this would result in an inorganic carbon production rate of 126 mg/l which is 49 mg/l larger than the measured value.

Steady-State Performance

Steady-state analysis was conducted on the feed substrate and all column effluents for the period extending from day 457 to day 511 of continuous operation. A summary of the steady-state operating data for this phase of the experiment is presented in Table 20. These data once again indicate that a single-stage anaerobic activated carbon filter with an empty bed detention time of only 11.62 hours would provide reductions in (a) TOC of 84 percent;

(b) COD of 93 percent; and, (c) catechol removal efficiencies exceeding 99.15 percent.

Table 20. Average Steady State Performance Data for
400 mg/l Catechol Fed Reactor

Parameter	Influent Value	Parameter Value in Column Effluents			
		1	2	3	4
pH	7.4	7.12	7.22	7.22	7.28
TOC, mg/l	255	40	34	32	25
TIC, mg/l	85	81	79	74	67
COD, mg/l	940	65.6	54	51	55
Catechol, mg/l	400	<3.42	1.43	1.34	0.88
Gas Production, ml/day		815	136	0	0
Methane, ml/day		682	127	0	0
Carbon Dioxide, ml/day		53	9	0	0
Nitrogen, ml/day		80	0	0	0
Alkalinity, mg/l as CaCO ₃	1920	1914	1837	1925	2035
NH ₃ -N, mg/l	53	25	40	59	30
TKN, mg/l	-	43	27	23	30
ORP	-	-230	-50	-	-

In addition, the process was producing an 84 percent by volume methane gas. The percent by volume of methane resulting from this phase of the experiment is slightly less than that obtained during the first phase of the experiment; this due to the increased feed organic carbon content which results in increased total CO₂ production and consequently an increased carbon dioxide fraction in the gas phase.

The concentration of total and volatile suspended solids in the individual column and clarifier effluents were measured on days 360 and 464 and are presented in Table 21.

Table 21. Effluent Solids Concentrations from Individual Columns and Clarifiers

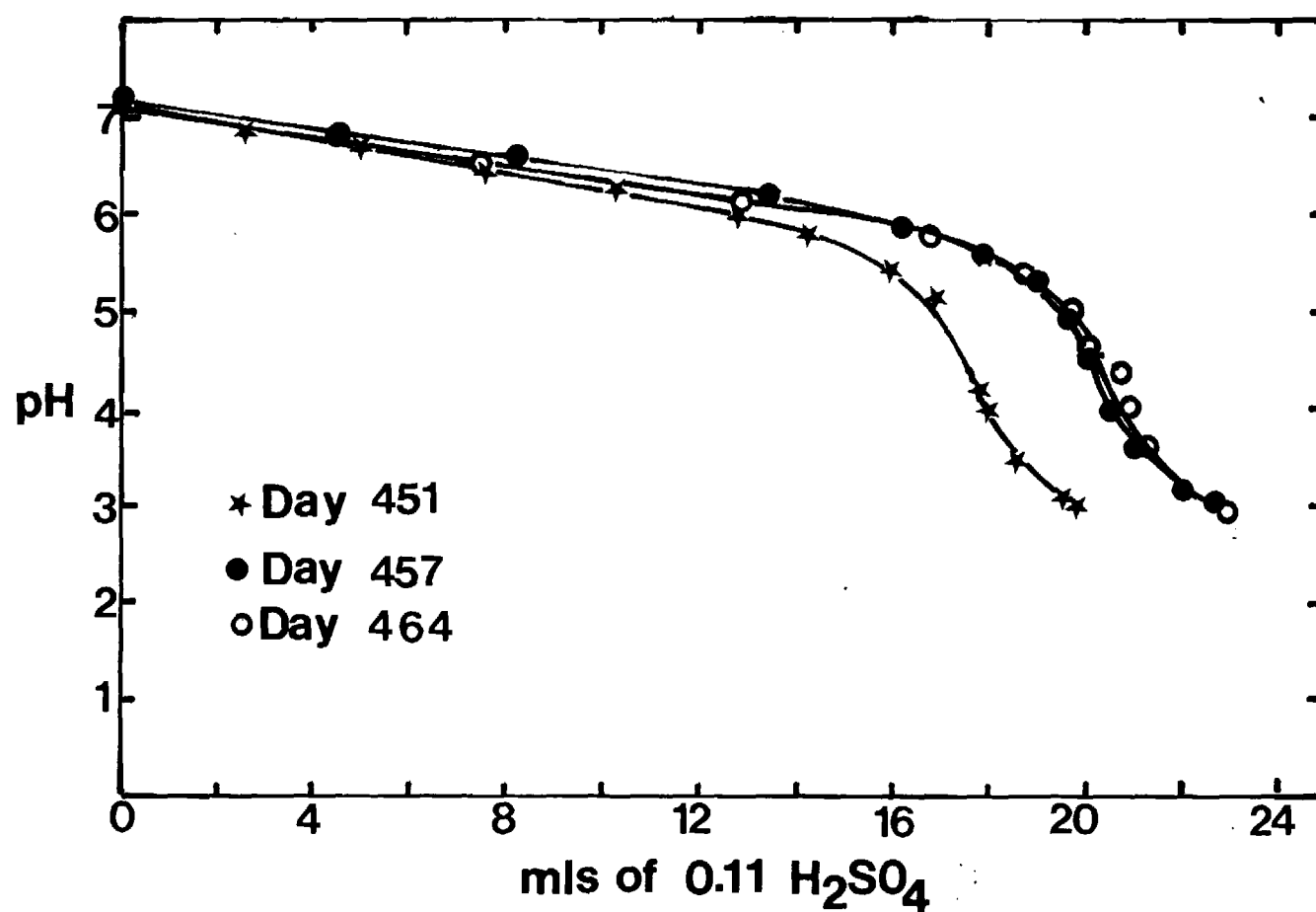
Effluent from	Day 360		Day 464	
	TSS (mg/l)	VSS (mg/l)	TSS (mg/l)	VSS (mg/l)
Column 1	738	485	524	248
Clarifier 1	263	114	33	4
Column 2	452	274	55	4
Clarifier 2	46	21	37	6
Column 3	58	36	32	6
Clarifier 3	350	282	40	0
Column 4	137	91	22	2

With the exception of the first column effluent, the suspended solids concentration in the effluents from the remaining three columns and three clarifiers were reasonably low indicating that the treatment system exhibited good overall removal efficiencies.

The alkalinity varied very little across the reactors during the period of intensive analysis varying between 1837 and 2255 mg/l as CaCO_3 . The titration curves shown in Figures 45, 46, 47 and 48 show once again that the treatment system did not alter the buffer capacity of the system indicating the absence of a major concentration of volatile acids in the effluent flows.

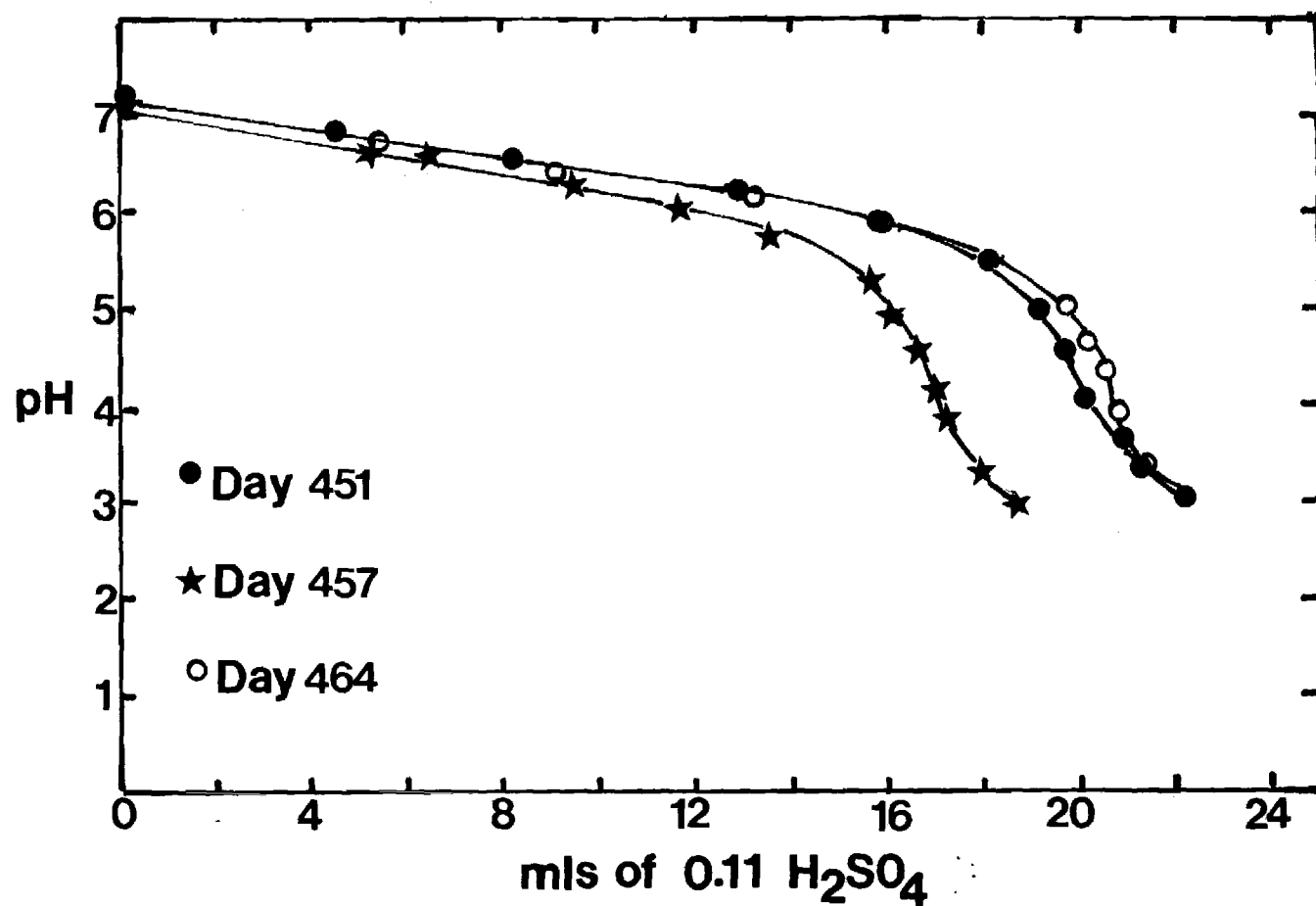
Phase III, 1000 mg/l Catechol

In the last phase of this experiment, the performance of the anaerobic activated carbon filter in treating a synthetic wastewater bearing 1000 mg/l of catechol was examined for a period of 47 days. During this phase of the experiment, the feed substrate was prepared daily in 4 l batches using 50 ml of the salt solution, 80 ml of the phosphate buffer solution, 4.0 g of catechol and distilled water. The theoretical feed COD and TOC computed using the



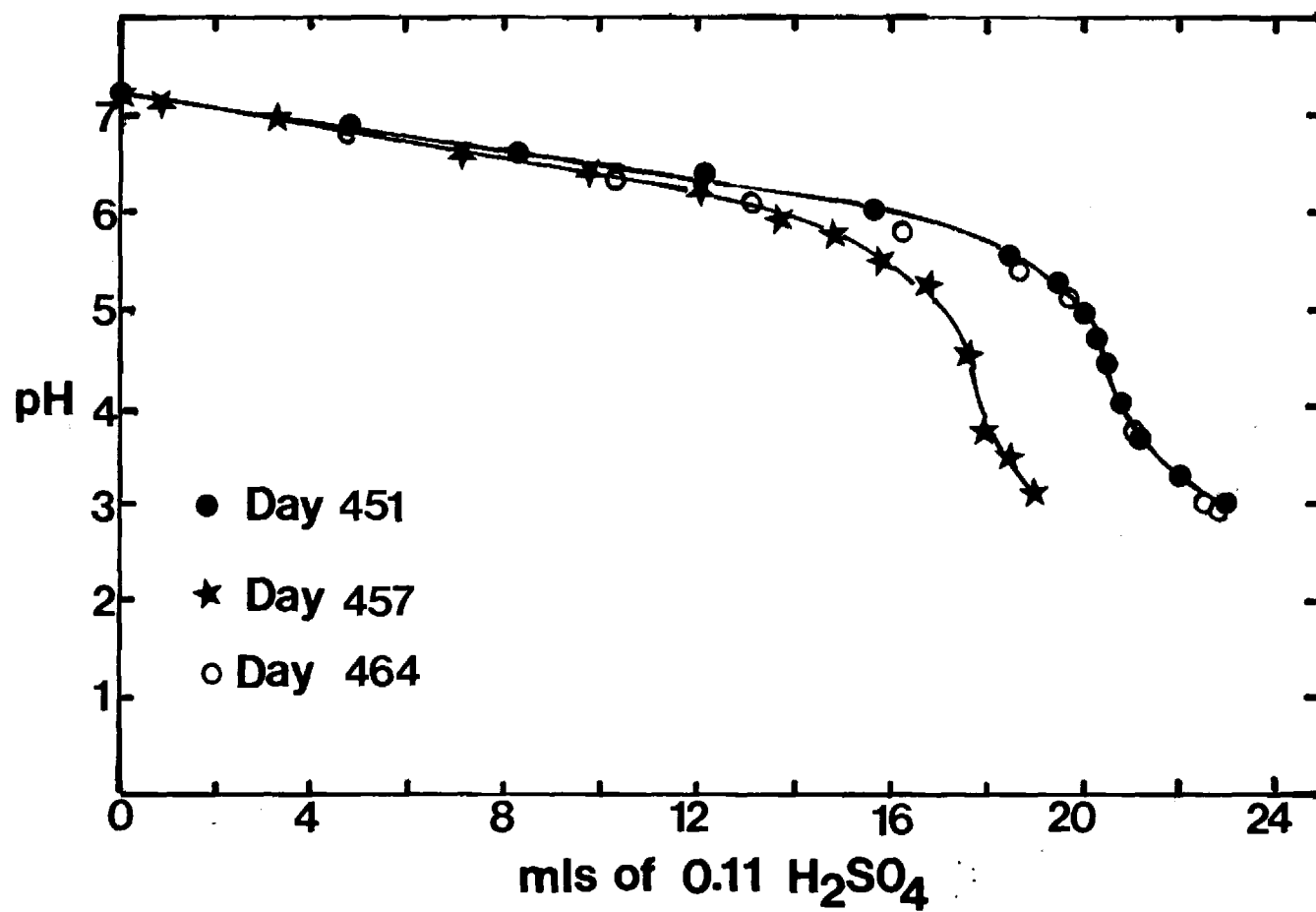
II. BUFFERING CAPACITY OF EFFLUENT FROM CATECHOL COLUMN ONE

FIGURE 45



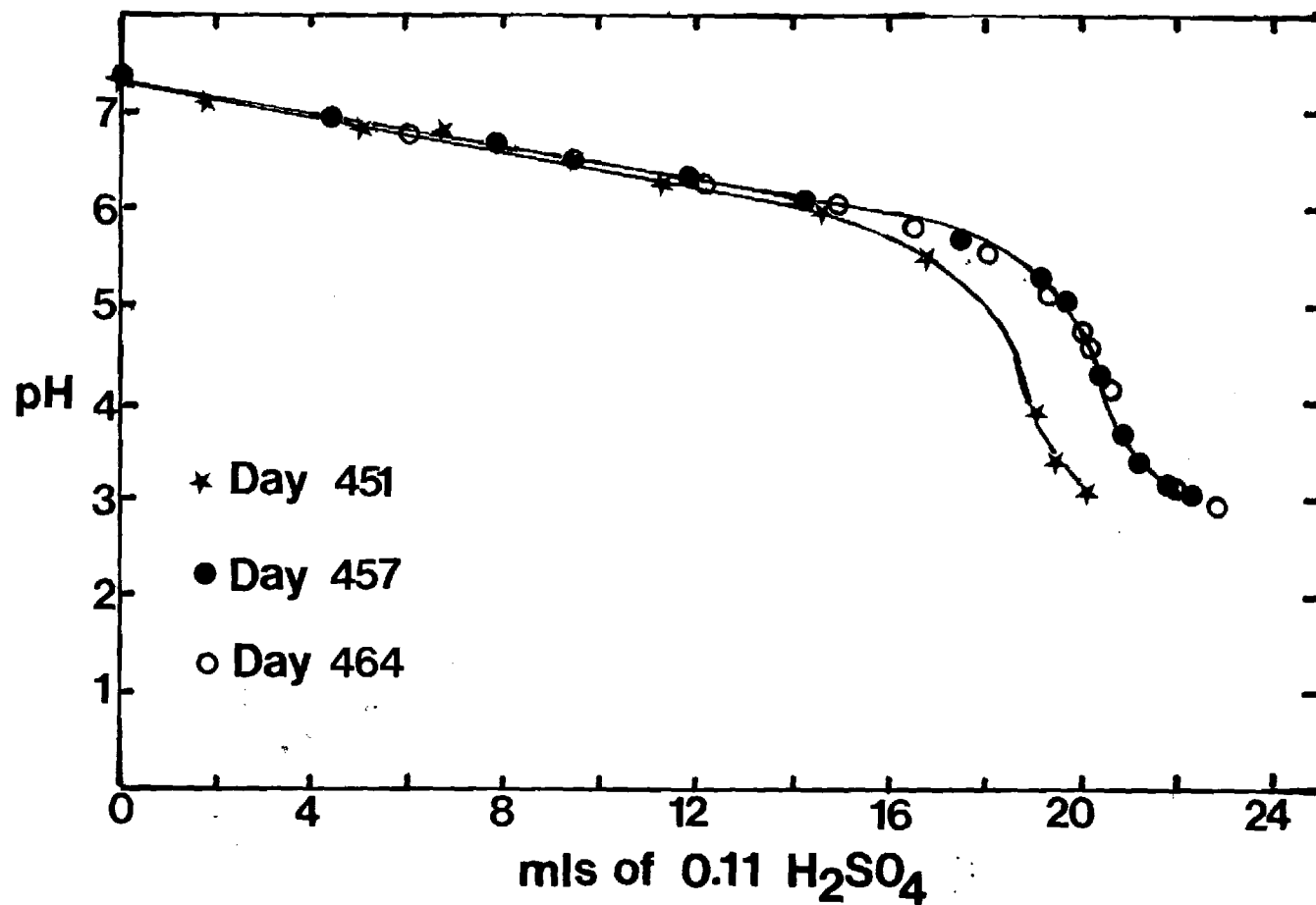
II. BUFFERING CAPACITY OF EFFLUENT FROM CATECHOL COLUMN TWO

FIGURE 46



II. BUFFERING CAPACITY OF EFFLUENT FROM CATECHOL COLUMN THREE

FIGURE 47



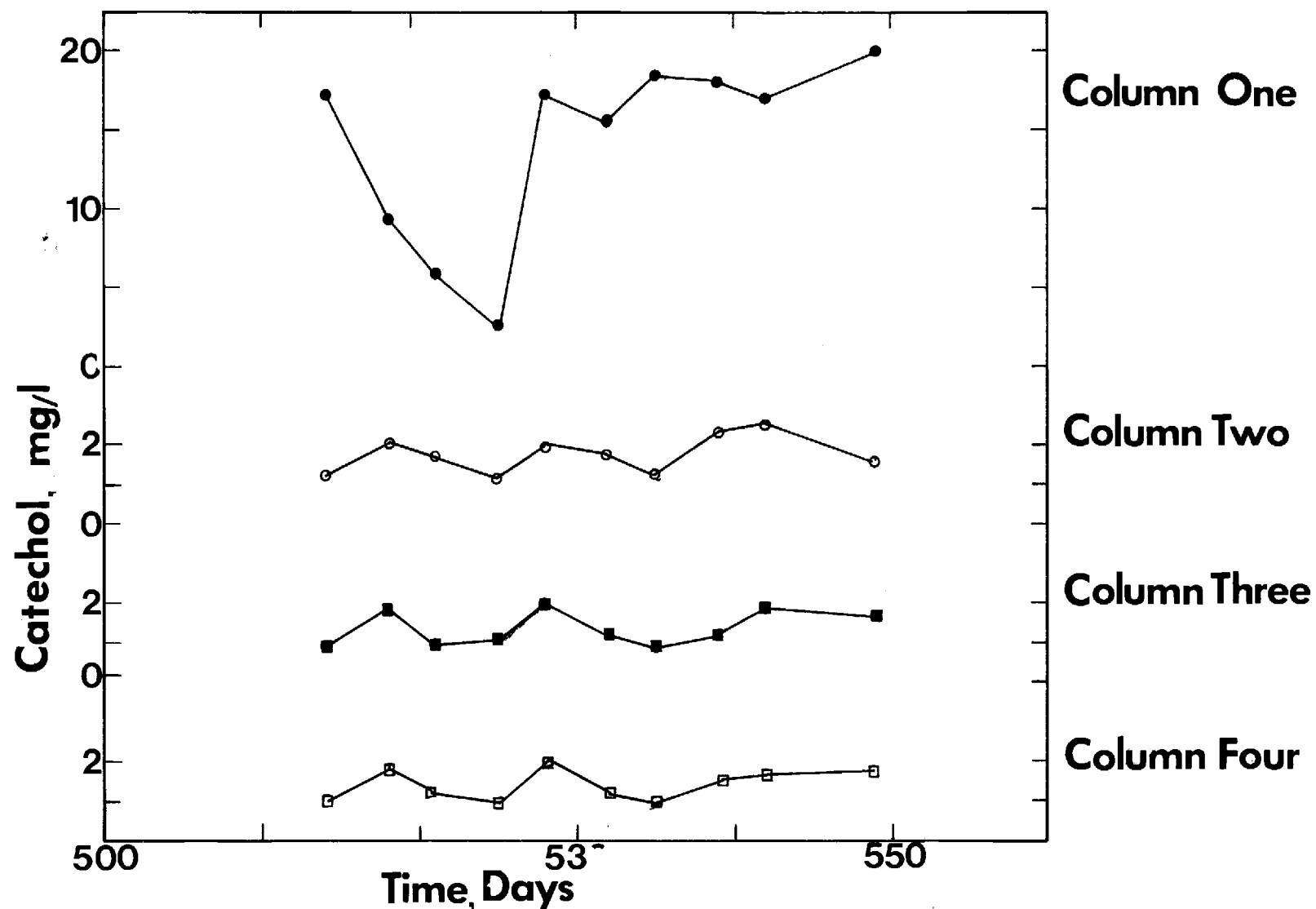
II. BUFFERING CAPACITY OF EFFLUENT FROM CATECHOL COLUMN FOUR

FIGURE 48

measured values for the salt solution and the theoretical values for catechol given in Table 15 were 2212 and 738 mg/l, respectively. The measured values of the two parameters COD and TOC in the feed as obtained from the average of 10 duplicate readings were 2165 and 758 mg/l, respectively. These computations and measurements yield a computed COD to TOC ratio of 3.00 and a measured ratio of 2.86. The feed substrate flow rate and recirculated flow were maintained at the same levels that were used in the first two phases of the experiment, namely 2 and 50 ml/min, respectively. The pH of the feed substrate was adjusted during the course of this phase of the experiment from an initial value of 7.45 to a final value of 7.55. The feed substrated was adjusted in this fashion in order to maintain as close to a neutral pH as possible throughout the experimental system. The ranges pH observed in the individual column effluents were 6.84 to 7.06 for column 1, 6.89 to 7.08 from column 2; 6.97 to 7.13 for column 3; and 6.96 to 7.13 from column 4.

The general response of the first column to an increase in the feed concentration of catechol was an immediate increase in the rate of gas production indicating that no additional acclimation period was needed and no shock effects were encountered. However, although gas production from the first column increased immediately as a consequence to the increased feed strength, a major portion of the organic carbon was not accounted for even at the end of this phase of the study indicating that active adsorption and biomass production were still occurring at the termination of this experiment.

Catechol Reduction. The concentration of catechol found in the individual column effluents is presented in Figure 49 for the duration of the third phase of this experiment. Absorbance at 268 nm was used to measure the concentration of catechol and because of the interference presented by other residual organics,

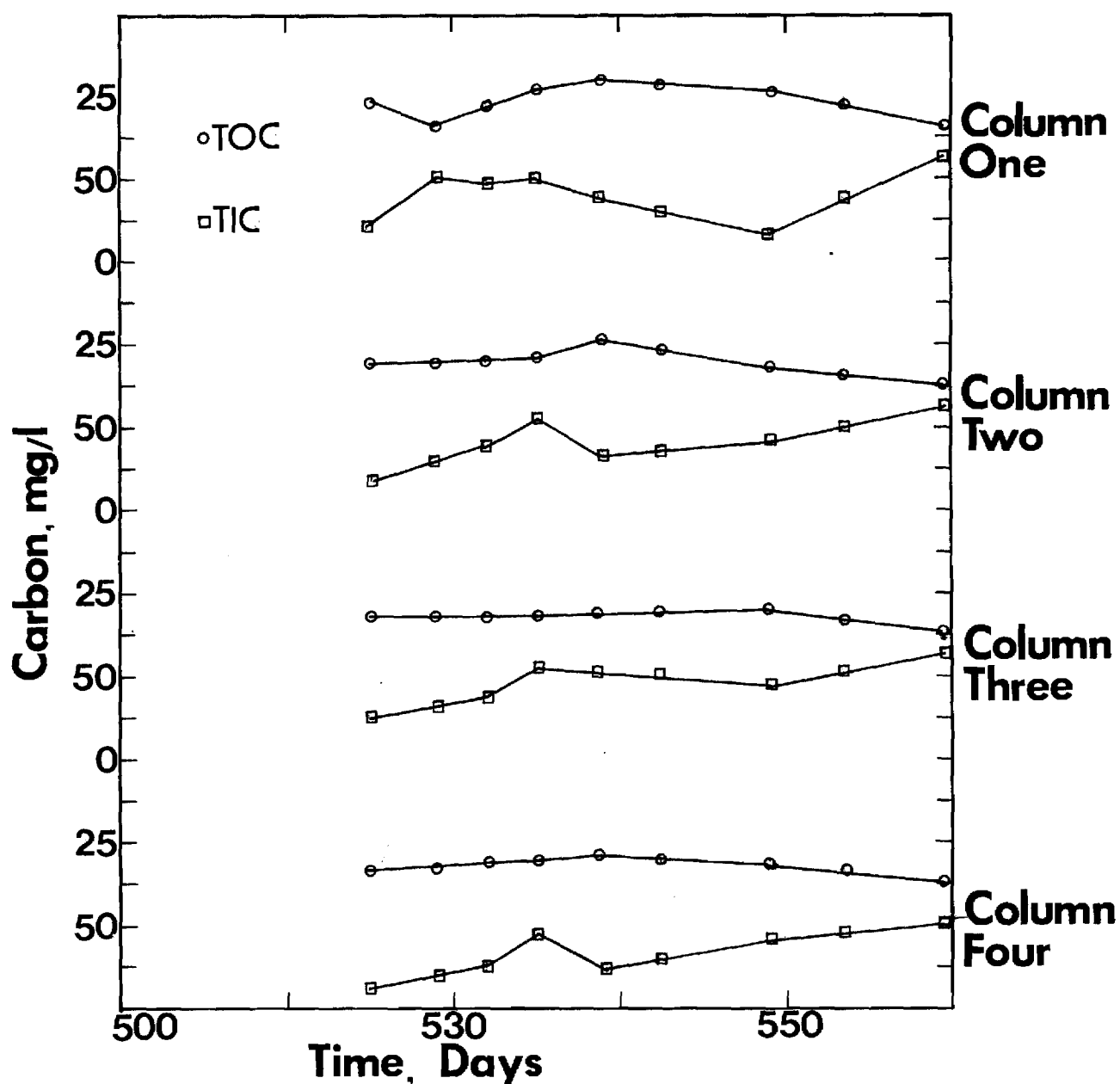


**Catechol Concentrations Of Individual Column
Effluents From Catechol Fed Reactor
Figure 49**

all values reported in Figure 49 are greater than the actual concentrations of this phenolic compound. The measured catechol concentrations ranged from a high of 20 mg/l to a low of 2.6 mg/l in the effluent from the first column resulting in catechol removal efficiencies in that column consistently greater than 98 percent. The concentration of catechol in the effluents of the three remaining columns ranged from 1.3 to 2.6 mg/l from the second column, 0.9 to 2.0 from the third column, and 1.0 to 2.0 from the fourth column. This corresponds to an overall catechol removal efficiency consistently exceeding 99.8 percent.

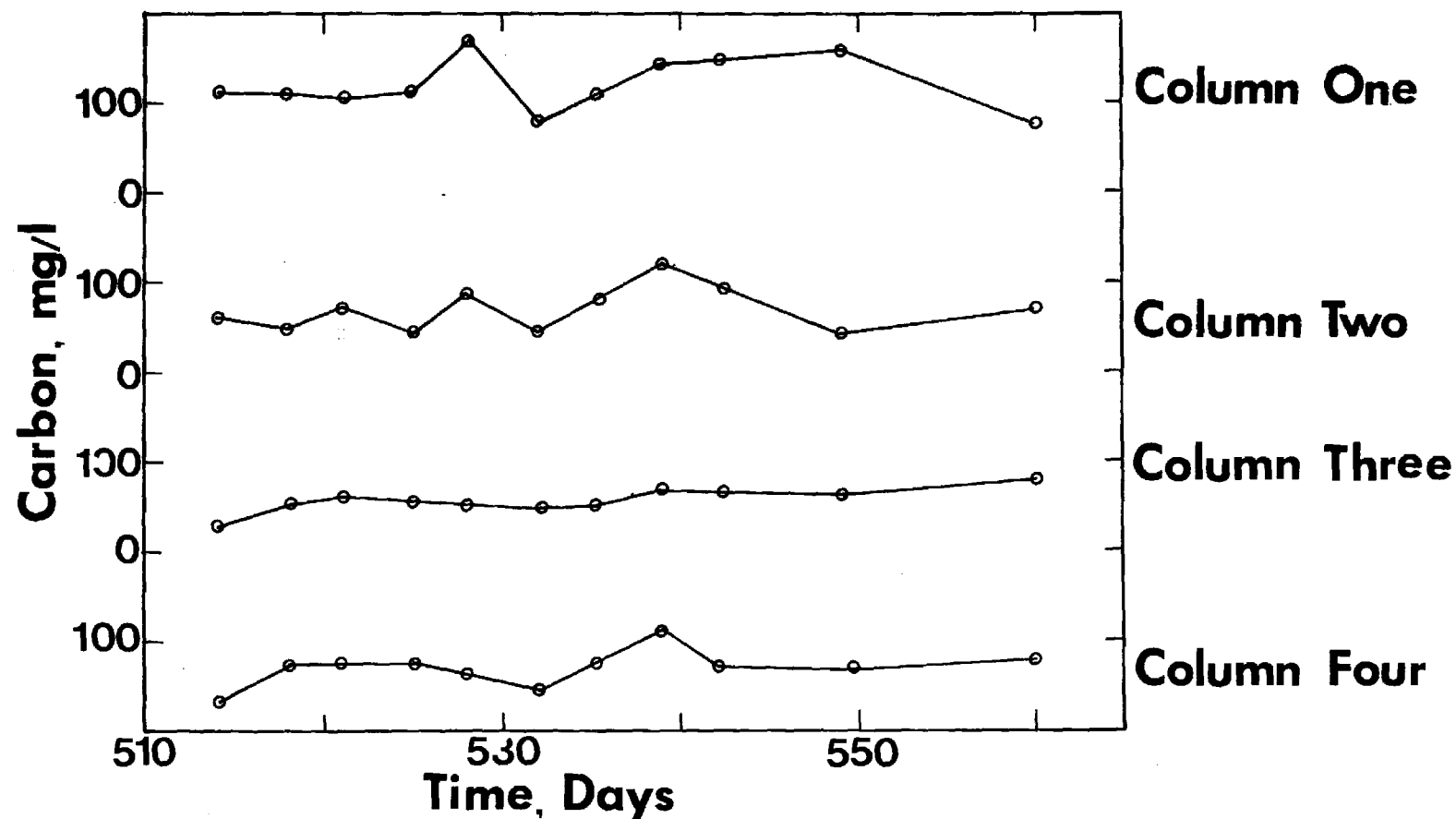
Organic and Inorganic Carbon. The organic and inorganic carbon content of the effluents from all four anaerobic filter columns is presented in Figure 50 for the duration of this phase of the experiment. The average TOC in the feed was 758 mg/l while the average organic carbon content of the effluent from the first column was 43 mg/l corresponding to an average organic carbon removal efficiency in the first column of 94 percent. The average organic carbon contents of the remaining three columns were 29, 23, and 25 mg/l which correspond to cumulative removal efficiencies of 96, 97 and 97 percent.

Chemical Oxygen Demand. The chemical oxygen demand of the individual column effluents for the duration of this phase of the experiment is shown in Figure 51. The influent COD averaged 2165 mg/l while the average COD of the effluent from the first column was 126 mg/l resulting in an average COD removal efficiency of 94 percent across the first column. The average COD values measured in the effluents of the remaining three columns were 68 mg/l for column 2; 55 mg/l for column 3; and 64 mg/l for column 4. Once again the first column was responsible for practically all the COD removal accomplished in the treatment process.



TOC, TIC Concentrations Of Individual Column Effluents From Catechol Fed React.

Figure 50



COD Of Individual Column Effluent From
Catechol Fed Reactor

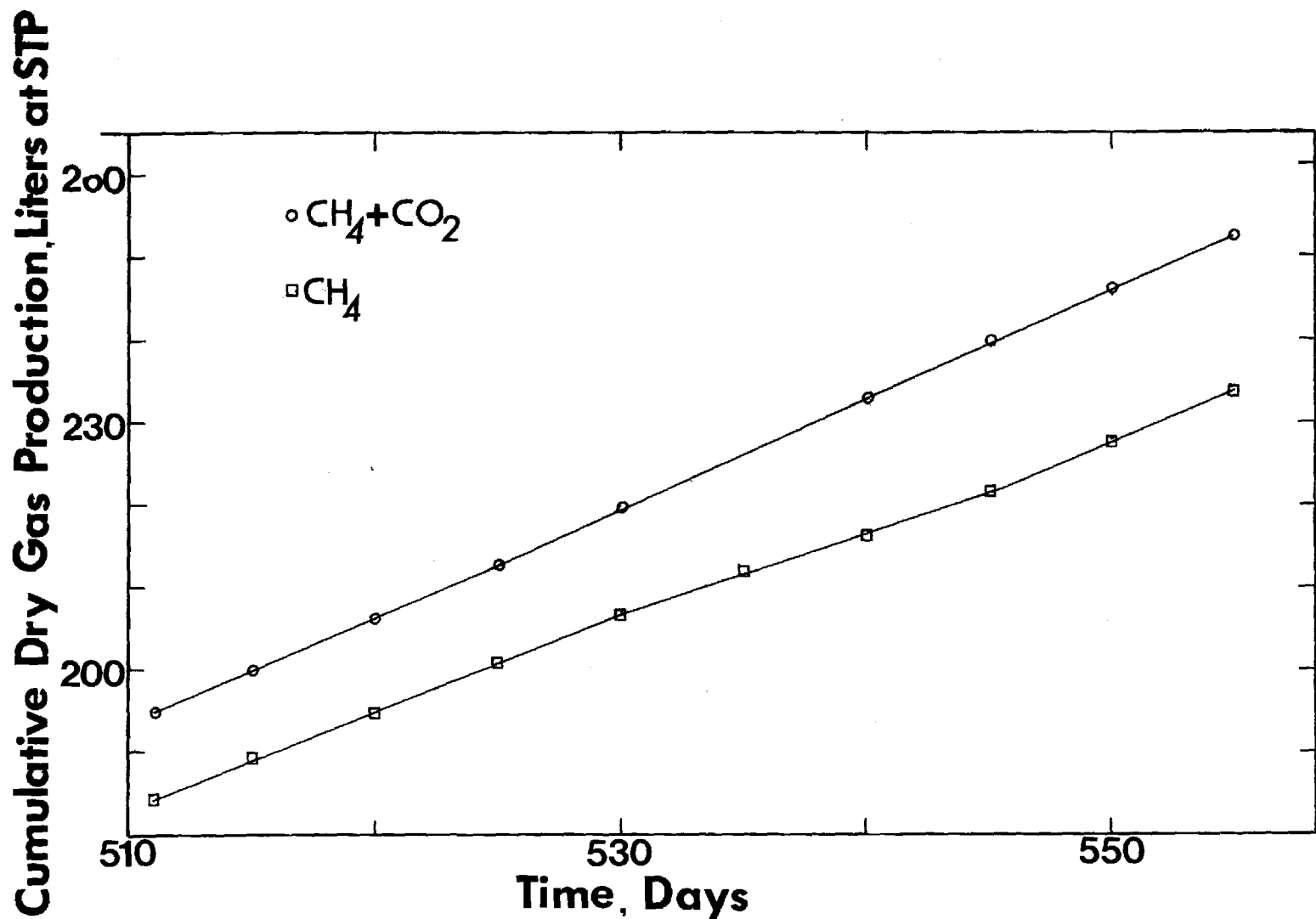
Figure 51

Gas Production. The cumulative total gas produced from the two columns that registered gas production, columns 1 and 2, and the total cumulative gas produced by the experimental reactor are presented in Figures 52, 53 and 54. The rate of gas production increased immediately after the feed catechol concentration was raised from 400 mg/l to 1000 mg/l. Corresponding to this increase in the feed substrate concentration, gas production increased from a steady-state production rate of 735 ml/day to a new rate of 1408 ml/day. This rate of gas production from the first column persisted throughout this phase of the experiment.

No appreciable gas production was observed from the second column until day 530 after which the second column was responsible for the production of 140 ml of gas per day. The average methane content of the gas produced in the first column was 94.3 percent while the methane accounted for 95.4 percent of the gas released from the second column.

A carbon material balance across the experimental system was constructed for day 550 of continuous operation (see Figure 55). As the data in Figure 53 indicate, 46.53 percent of the feed carbon content was not accounted for. This fraction of carbon, which amounts to 349 mg/l, is too high to attribute to biological growth and adsorption onto the carbon surface especially since no steady increase in the organic content of the effluent from the first column was noted.

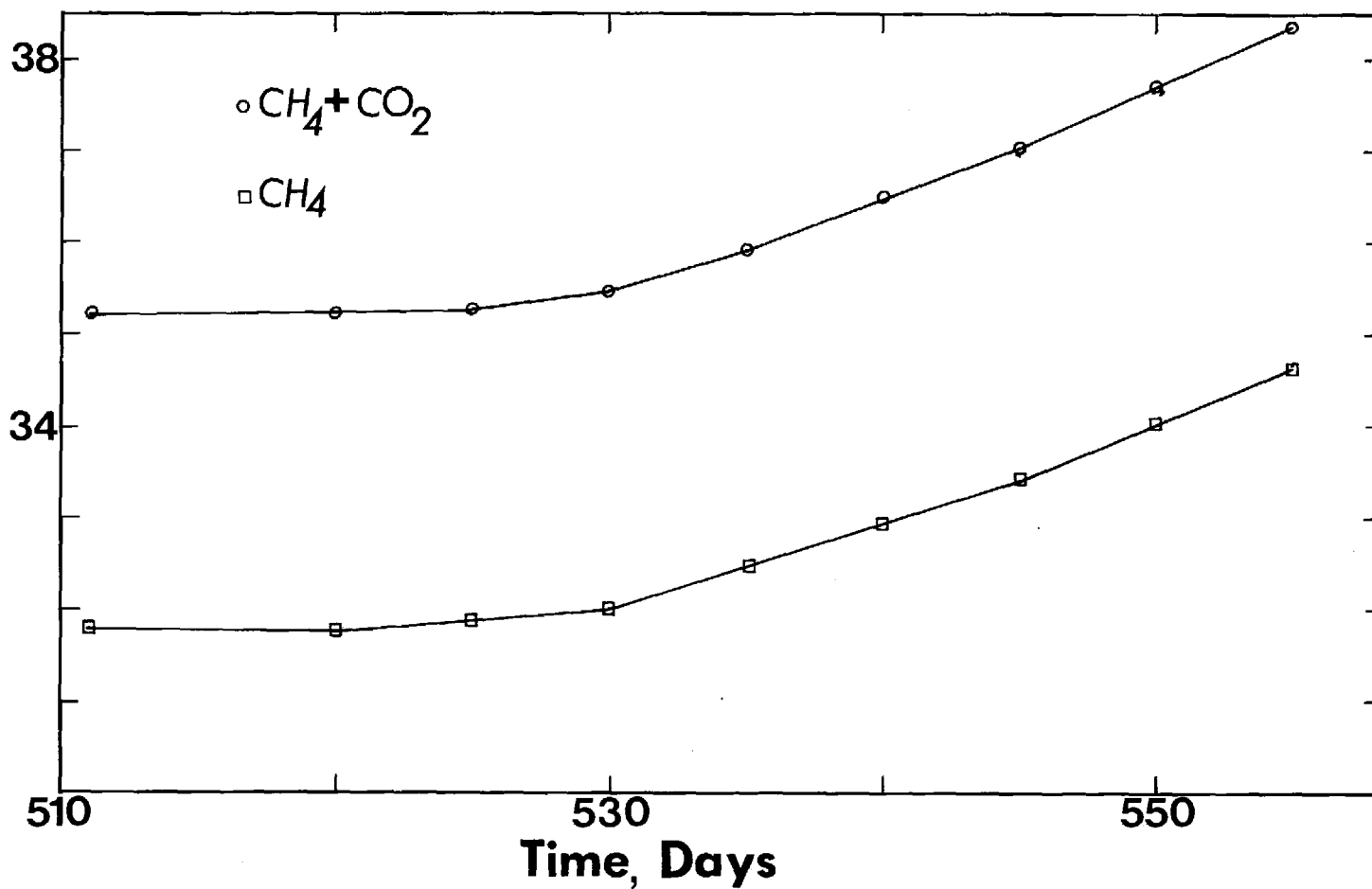
Healy et al. (1977) stated that the anaerobic degradation of catechol should result in the conversion of the organic carbon of catechol to methane gas and aqueous and gaseous carbon dioxide in the ratio of 54.17 and 45.83 percent. The methane gas liberated from the treatment process accounted for 73.6 percent of the total methane and gaseous and aqueous carbon dioxide



Total Gas Production, Column One Catechol Fed Reactor
1000 mg/l

Figure 52

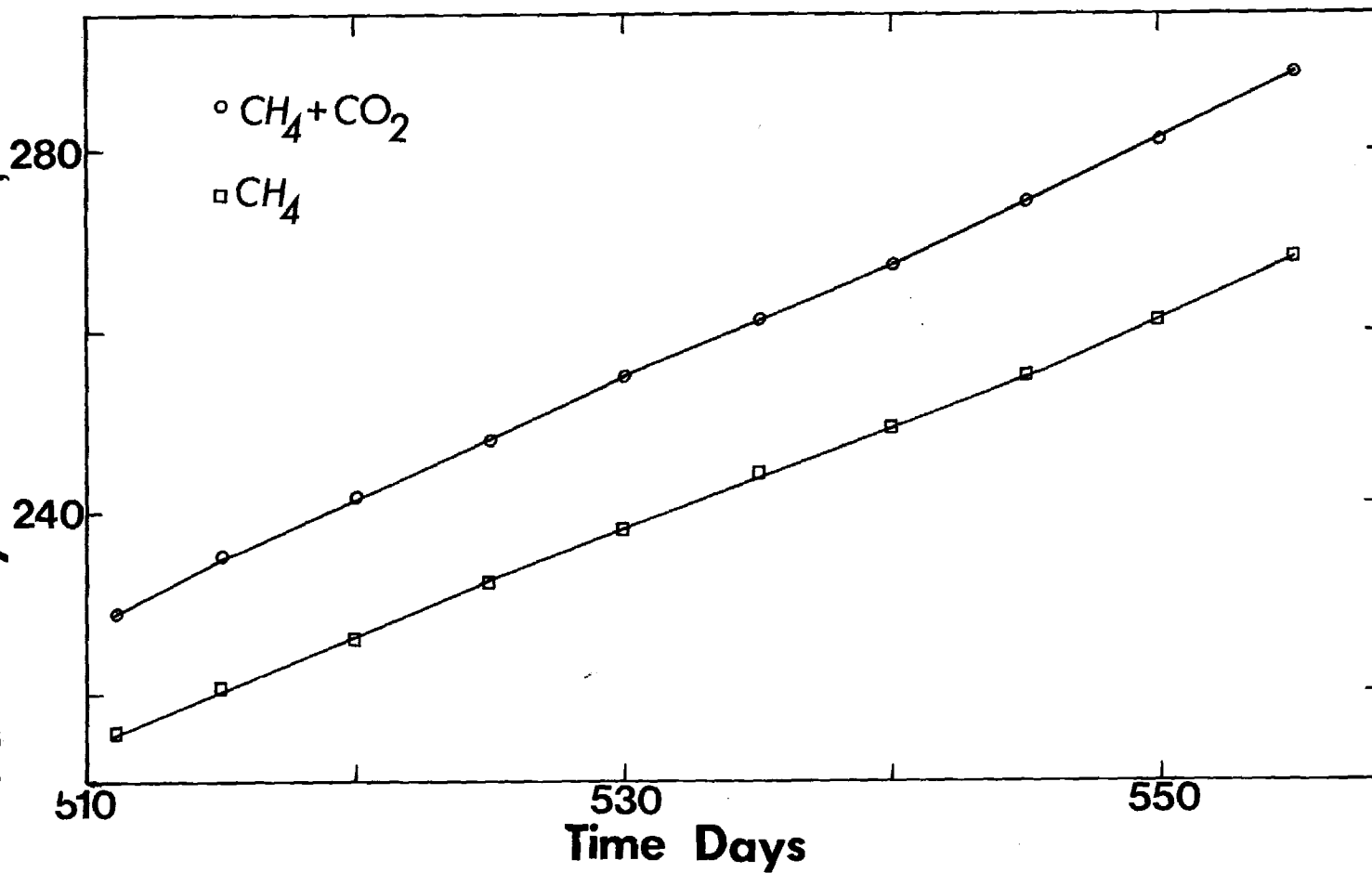
Cumulative Dry Gas Production, Liters at STP



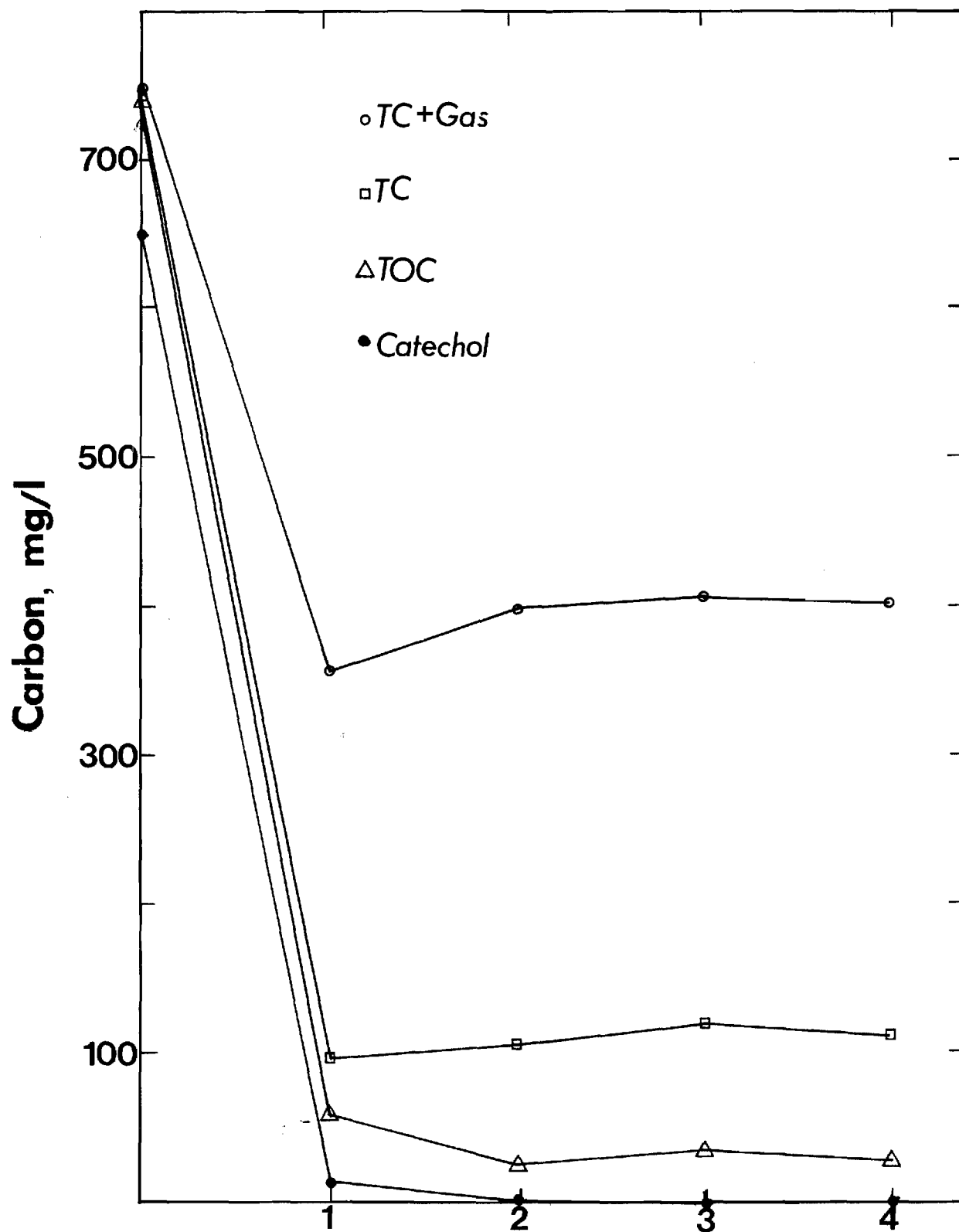
Total Gas Production, Column Two Catechol Fed Reactor
1000 mg/l

Figure 53

Cumulative Dry Gas Production, Liters at STP



Total Gas Production, Column One and Two Catechol
Fed Reactor, 1000 mg/l
Figure 54



Column Number
Day 550
Carbon Balance Across Catechol Fed Reactor
1000 mg/l
Figure 55

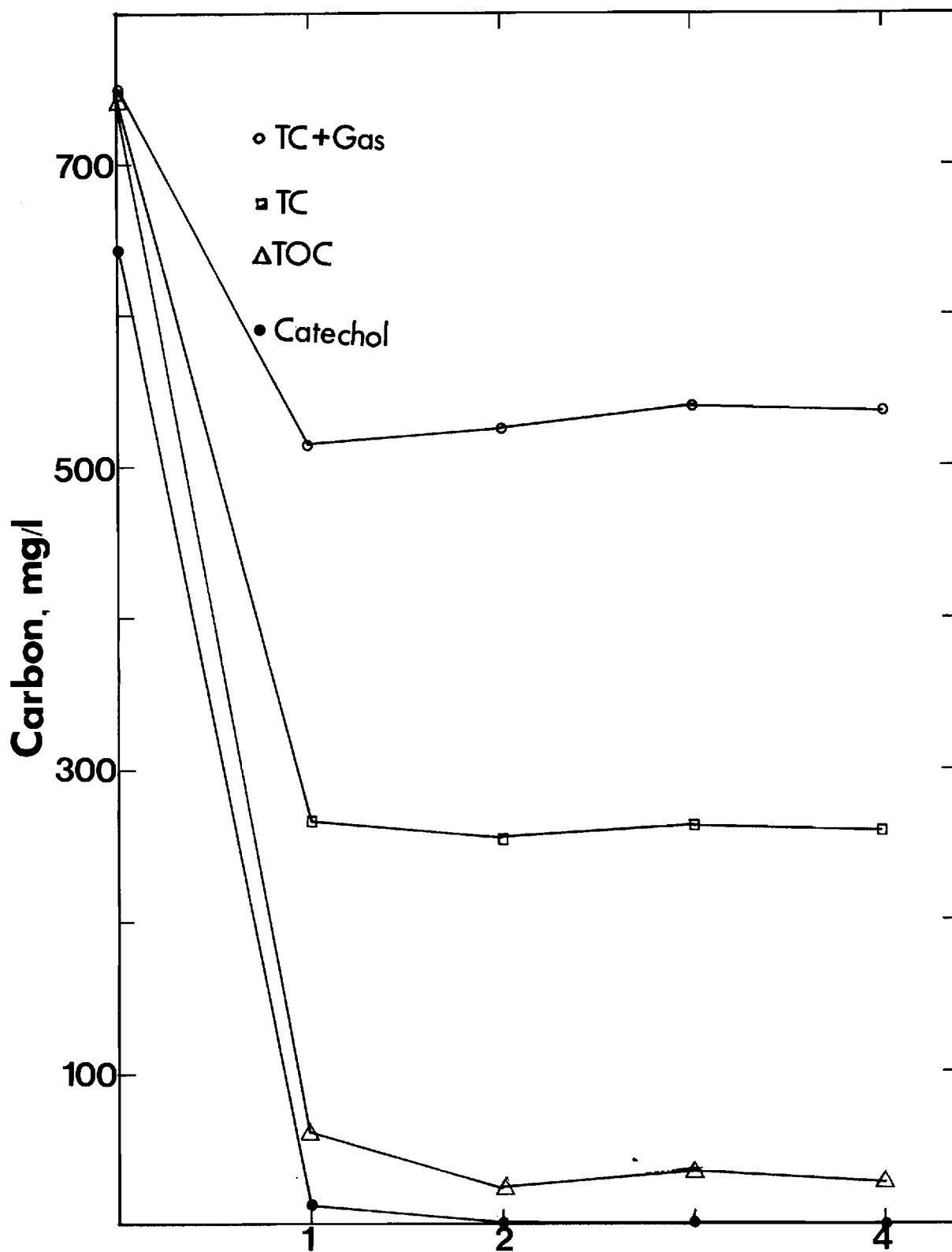
(see Figure 53). In order to investigate the integrity of the TIC measurement, a series of 10 samples were analyzed for TIC by splitting each sample into two portions and filtering one sample prior to analysis for TIC while the other sample was analyzed in the unfiltered form. The results from this experiment indicated clearly that a major fraction of the TIC was lost during filtration. The fraction of TIC lost during this procedure increased with increasing TIC values and it ranged from 10 to 150 percent of the TIC value in the filtered samples. Using this fact, a new carbon material balance was constructed across the treatment system in which the gaseous carbon dioxide and TIC were assumed to be equal to 84.6 percent of the carbon equivalent of the methane gas produced (see Figure 56). Using this approach, 72 percent of the feed carbon may be accounted for, while the remaining 35 percent could be attributed to biomass production and adsorption.

This phase of the experiment is still under continued operation and once steady state operating conditions are attained, the results will be made public through publication in technical journals.

Treatment of O-Cresol Bearing Substrate

The o-cresol fed experimental reactor was operated continuously for a period of 405 days. During the first 10 days of continuous operation, the feed o-cresol concentration was maintained at 100 mg/l. The o-cresol content of the feed was increased to 200 mg/l for the period extending from day 31 to day 170 of continuous operation. The feed o-cresol concentration was later increased to 256 mg/l. This feed concentration was finally selected because it corresponds to 1 ml of o-cresol in 4 l of substrate solution.

The feed o-cresol substrate was prepared daily in 4 l batches using 17 ml of the salt solution, 34 ml of the phosphate buffer, an appropriate



Column Number
Day 550

Carbon Balance Across Catechol Fed Reactor
1000 mg/l
Figure 56

volume of o-cresol, and distilled water. The theoretical COD and TOC of the feed substrates and the average measured values corresponding to the three o-cresol feed concentrations are given in Table 22.

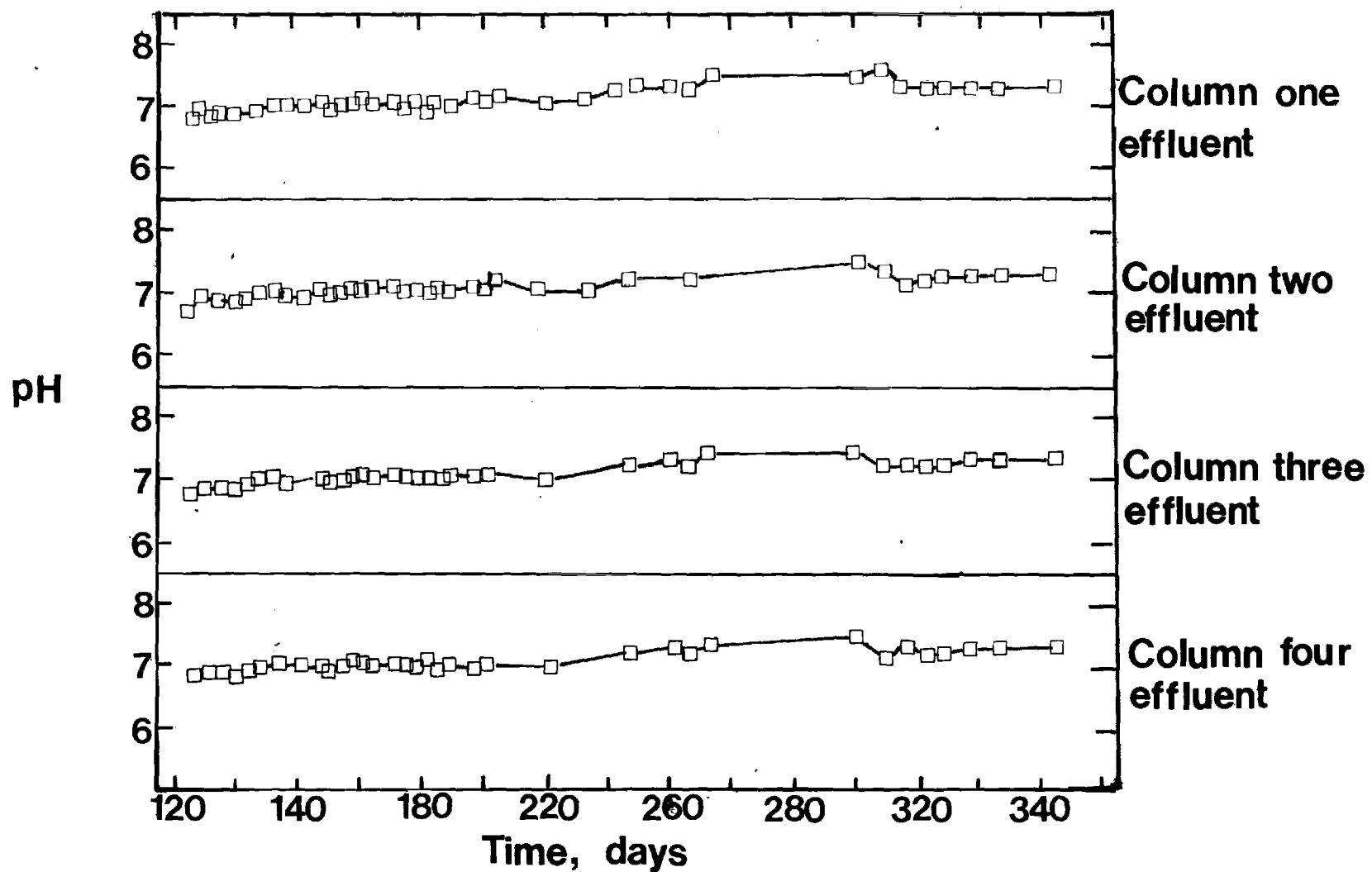
Table 22. Computed and Measured TOC and COD of O-Cresol Feed Substrate

Period (days)	O-Cresol Concentration (mg/l)	COD		TOC	
		Computed (mg/l)	Measured (mg/l)	Computed (mg/l)	Measured (mg/l)
0-30	100	361	325	106	98
31-170	200	613	543	183	172
171-405	256	754	660	227	214

The flow rate of the feed solution was maintained at 2 ml/min while the recirculation flow rate was set at 50 ml/min.

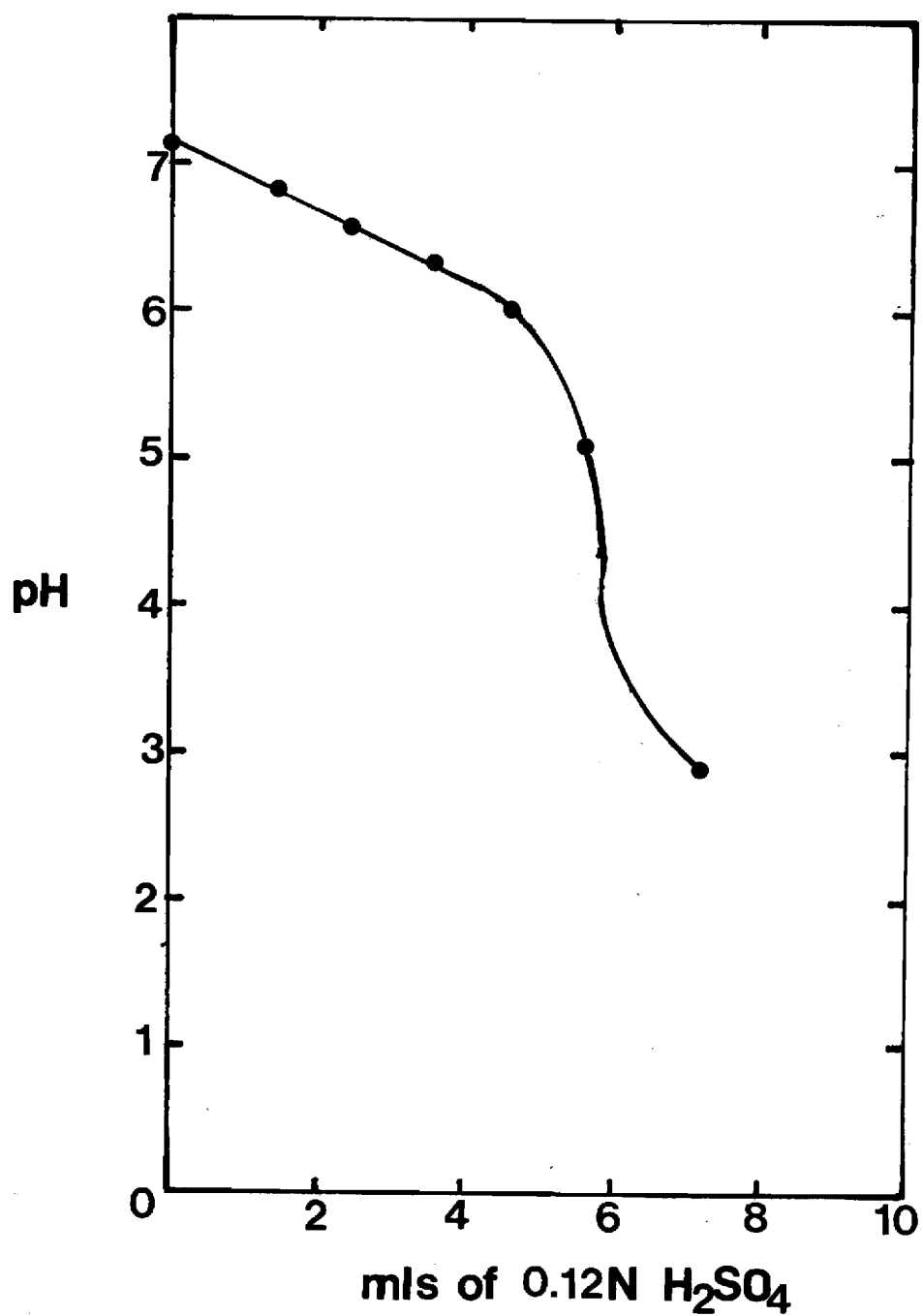
The pH of the feed substrate was initially maintained at 7.0 until day 259 when the pH in the feed was raised to 7.3 in an attempt to adjust for an anticipated increase in volatile acids production as a result of increased biological activity. The pH values in the individual column effluents during the course of this experiment are given in Figure 57. The titration curve of the feed substrate shown in Figure 58 indicates that this synthetic waste had a strong buffer capacity of 0.17 meq/l down to the lowest observed pH of 6.81. Measured pH values ranged from 6.81 to 7.58 throughout the columns while the pH ranges observed for the individual column effluents were 6.82 to 7.58 for column 1; 6.83 to 7.47 for column 2; 6.81 to 7.45 for column 3 and 6.81 to 7.45 for column 4.

Very limited biological activity was observed in the o-cresol fed anaerobic activated carbon filter. A number of attempts were made throughout the experiments in order to improve gas production from this reactor; these included



pH IN INDIVIDUAL COLUMN EFFLUENTS FROM O-CRESOL FED REACTOR

FIGURE 57



BUFFERING CAPACITY: 0-CRESOL INFLUENT FEED

FIGURE 58

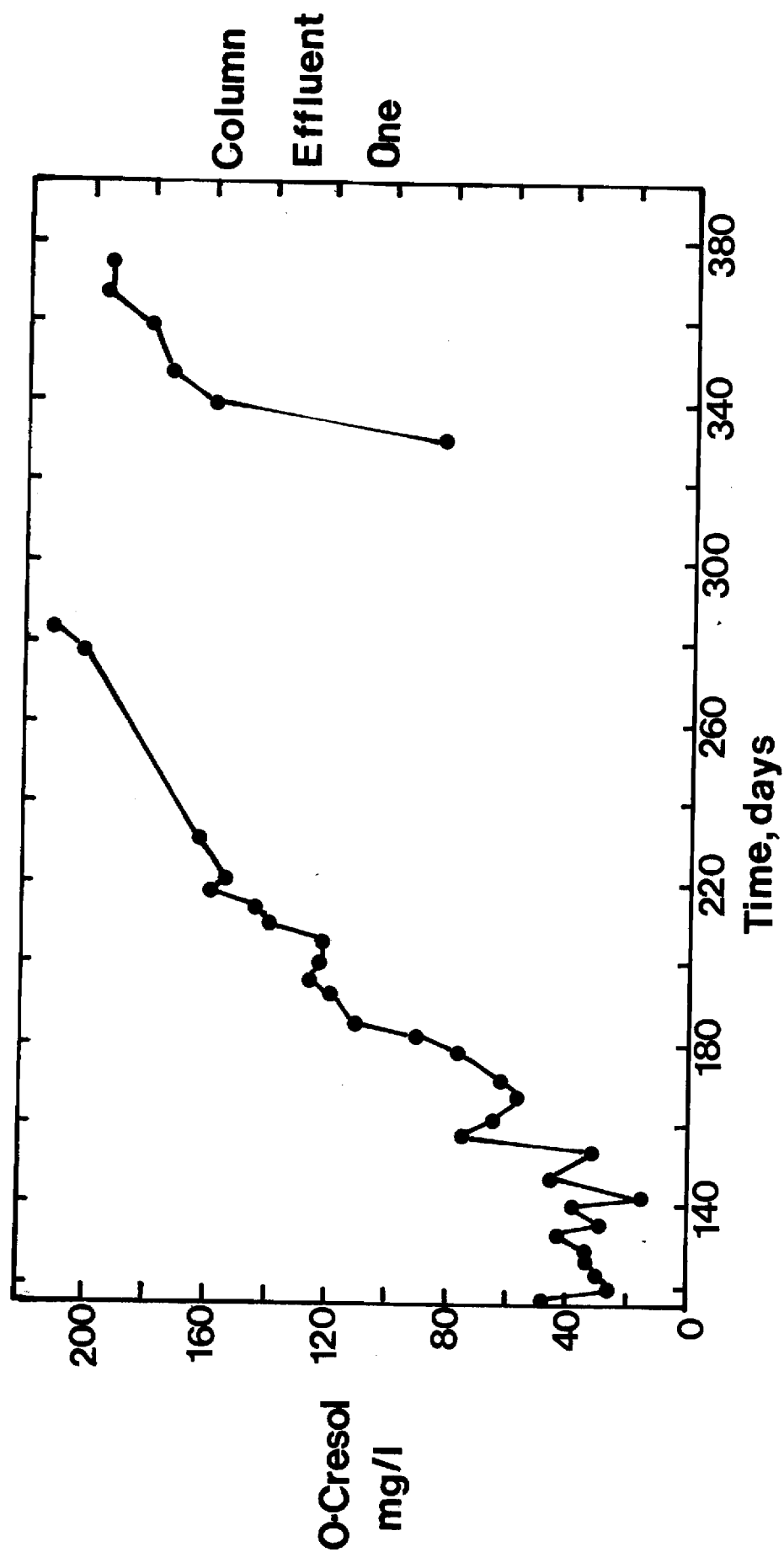
reseedings with anaerobic sludge digester supernatant, reseeding with a catechol acclimated sludge, and exposing the reactors to a hydrogen gas rich head space. All these attempts resulted in little or no improvement in the performance of the system in treating o-cresol.

O-Cresol Reduction. The concentration of o-cresol in the effluent from the first column followed a conventional breakthrough curve between day 120 and day 282. During this period and barring minor fluctuations, the effluent o-cresol content increased steadily from about 35 mg/l on day 120 to a value of 210 mg/l on day 282. At this point the column was reseeded with an o-cresol acclimated sludge and upon resumption in monitoring on day 330, the o-cresol concentration in the effluent from the first column had dropped to 80 mg/l. The effluent concentration, however, increased very sharply between days 330 and 340 where it finally levelled at 200 mg/l o-cresol.

A similar but delayed behavior was observed concerning the o-cresol content in the effluent from the second column which average 5 mg/l for the period extending between day 120 and day 235 and then increased sharply to a concentration exceeding 180 mg/l at day 360.

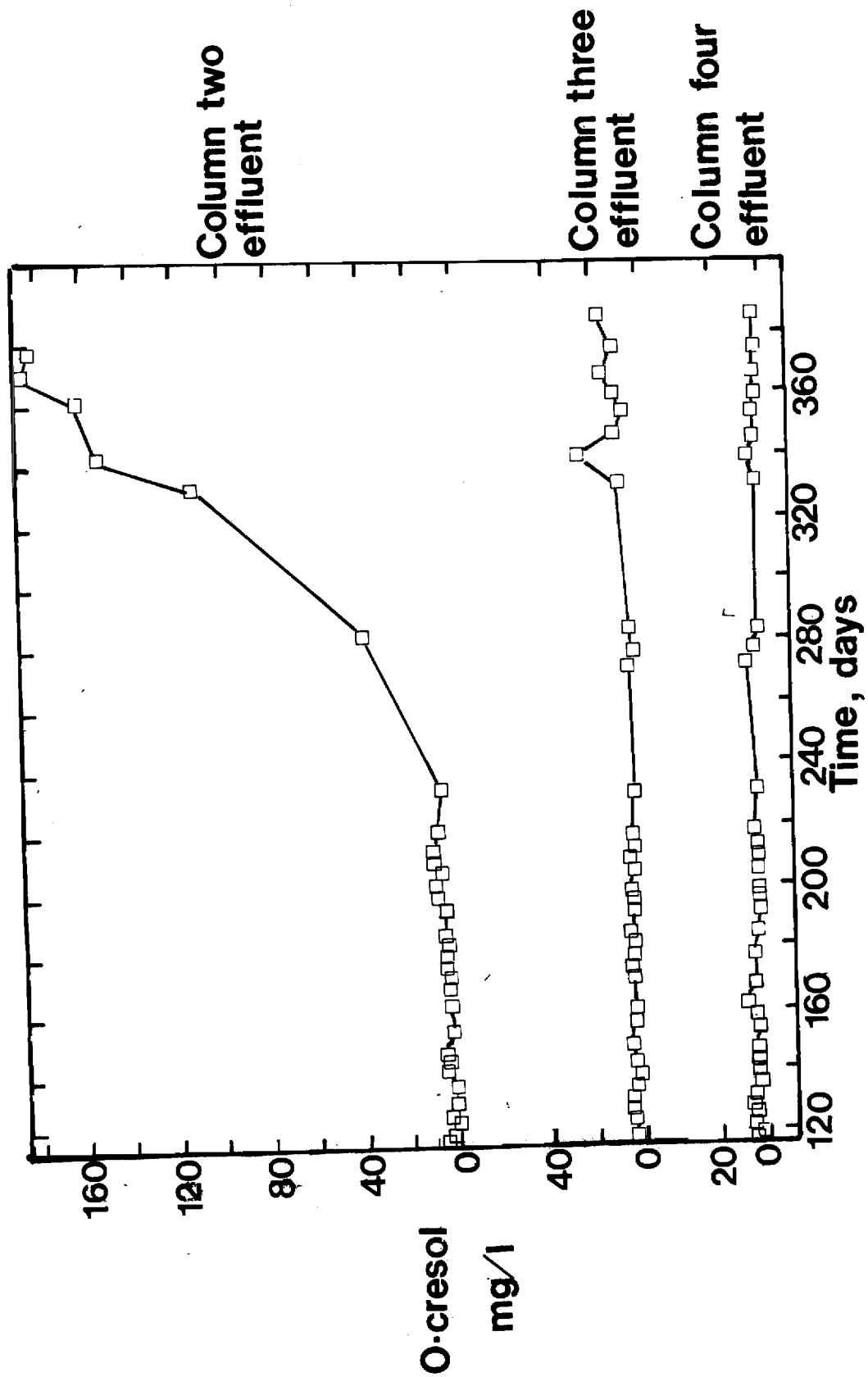
The o-cresol content in the effluents from the last two columns was consistently lower than 5 mg/l.

The o-cresol breakthrough data presented in Figures 59 and 60 suggest very strongly that adsorption onto the carbon surface may very well have been the primary removal mechanism for o-cresol. The adsorption capacity of Amoco powdered activated carbon for o-cresol from pure aqueous solutions of this compound has been reported to be 0.286 g o-cresol per g-carbon and 0.374 g-o-cresol per g-carbon for solution equilibrium concentrations of 200 and 256 mg/l, respectively (Singer et al., 1978). The effluent o-cresol concentration from



CONCENTRATION OF INDIVIDUAL COLUMN EFFLUENTS FROM
O-CRESOL FED REACTOR

FIGURE 59



CONCENTRATIONS IN INDIVIDUAL COLUMN EFFLUENTS FROM O-CRESOL
FED REACTOR

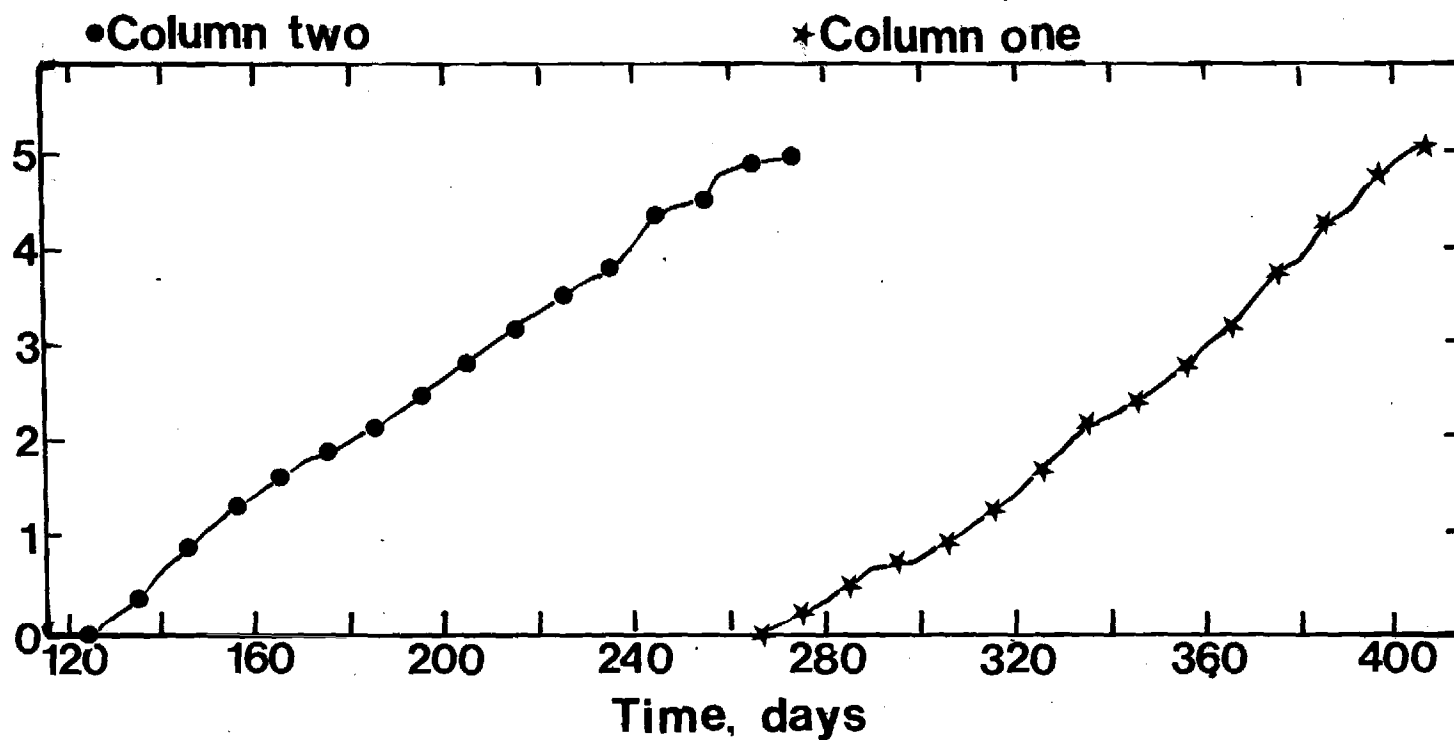
FIGURE 60

the first column reached a high of 210 mg/l on day 280 of continuous operation, by that time 169.8 g of o-cresol have been introduced into the reactor system and only 48.38 grams were found in the effluent from the first column (computed by integration under the curve in Figure 57 for the period between days 120 and 280). This results in a total removal of o-cresol of less than 153.8 g which when divided by the quantity of activated carbon charged into the first column results in a removal of 0.271 g-o-cresol/gram of carbon which corresponds very closely to the theoretical capacity of the carbon for adsorbing this phenolic compound. A similar analysis on the first two columns results in a removal of 0.266 g-o-cresol/g-activated carbon. These two capacity values fall very closely within the adsorption capacity ranged reported in the literature for o-cresol thus confirming the suspicion that adsorption onto the carbon and not biodegradation was responsible for the removal of o-cresol from the synthetic wastewater.

Gas Production. The anaerobic gas produced from every column reactor was collected separately and monitored for volume and composition. The cumulative dry methane and CO₂ produced from the different column reactors is plotted in Figure 61, while the total cumulative dry methane and CO₂ produced from the whole treatment system is plotted in Figure 62.

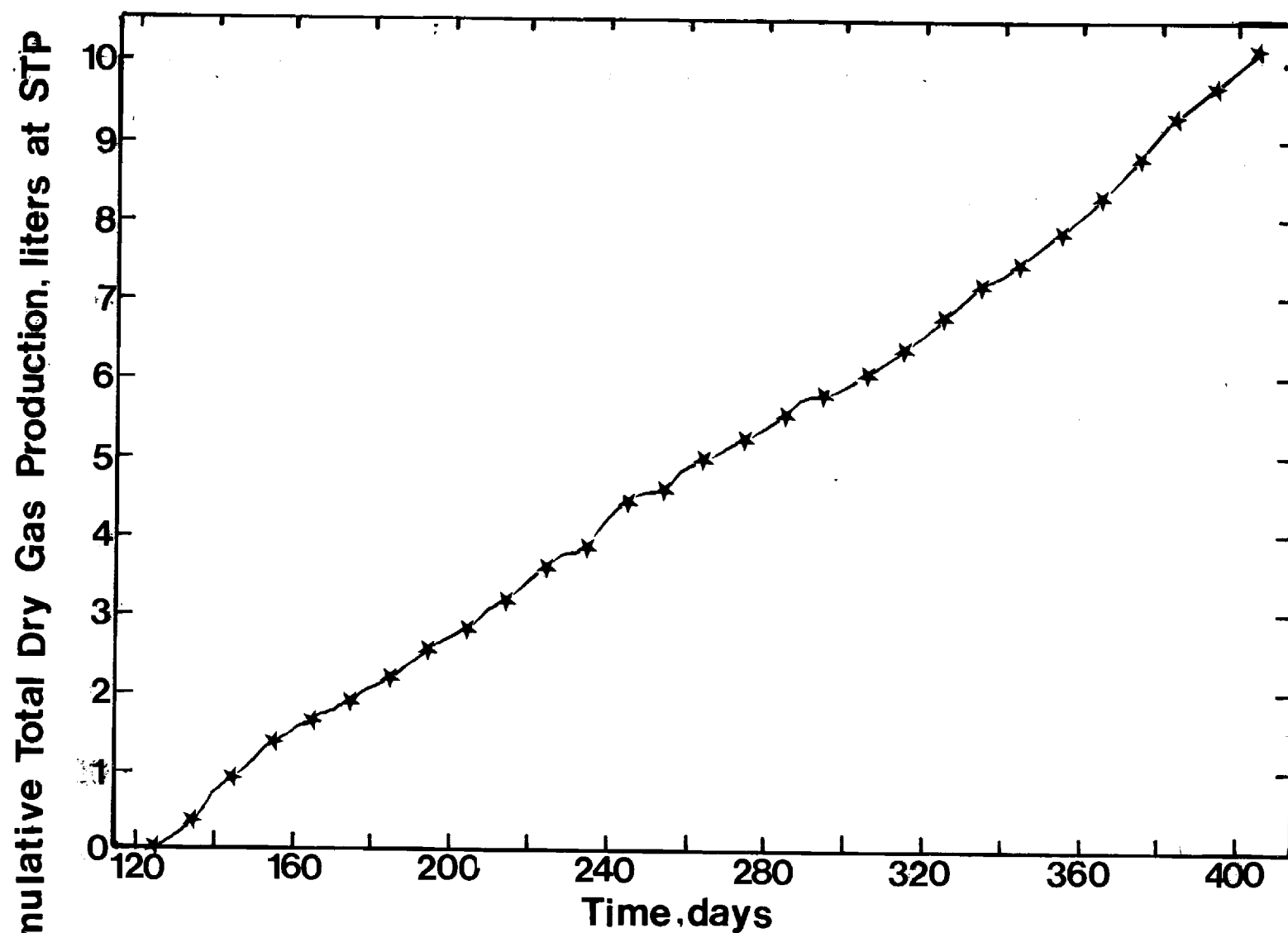
No measurable gas was produced from any of the columns during the first 120 days of continuous operation, however, on day 122 gas production was observed from the second column at a rate of 36.36 ml of methane and gaseous carbon dioxide per day which corresponds to 6.76 mg/l of carbon. Gas production from the second column persisted at the same rate until day 260 of continuous operation when gas production from this column ceased completely. On the same day of cessation of gas production from the second column, gas

Cumulative Total Dry Gas Production, liters at STP



TOTAL GAS PRODUCTION FROM O-CRESOL COLUMNS
ONE AND TWO

FIGURE 61



TOTAL GAS PRODUCTION FROM O-CRESOL FED REACTOR

FIGURE 62

started being produced from the first column which ultimately reached a steady rate of 42.3l ml of methane and carbon dioxide per day. This gas production rate is equivalent to 7.87 mg/l of carbon.

During the period of active gas production from the first column, the TIC in the effluent of this column average about 10.38 mg/l over the TIC in the effluent from the first column. This incremental value in TIC when added to the carbon equivalent of the gaseous products results in 17.14 mg/l of carbon which is very close to the TOC value in the feed substrate of 28.23 that is attributable to ethanol, sodium citrate and the vitamin extract. Similar analysis across the first column during the period between days 265 and 400 reveals that the carbon equivalent of the gas produced and the incremental TIC across the first column amount to 21.18 mg/l once more providing proof that no degradation of cresol was occurring.

SUMMARY AND CONCLUSIONS

The objective of this research was to develop a new wastewater treatment process for the treatment of refractory and toxic aromatic compounds commonly found in wastewater. Two experimental units were constructed each consisting of four anaerobic-activated carbon filters connected in series with clarification provided after each of the first three columns. Each column was equipped with a reversible recirculation pump in order to allow for the recirculation of the aqueous contents around each individual reactor.

The treatability of two phenolic compounds, catechol and o-cresol, in the anaerobic-activated carbon filter was assessed using different organic loading rates of the two phenols. Throughout the study, the experimental units were operated at a feed substrate flow rate of 2 ml/min resulting in a total empty bed contact time of 46.48 hours. The recirculation flow rate was set at 50 ml/min.

The catechol bearing substrate fed experimental reactor was operated continuously for a period of 557 days. During the first phase of this experiment, which lasted for 333 days, a synthetic substrate containing 200 mg/l of catechol and having a total organic carbon content of 139 mg/l and a chemical oxygen demand of 414 mg/l was fed to the first column of the reactor system. After an acclimation period of 120 days, the performance of the system in reducing the catechol in the feed improved steadily reaching steady state operating conditions after 250 days of operation. At steady-state, the experimental data indicate that a process consisting of one single column having an empty bed detention time of 11.62 hours was sufficient to efficiently treat the synthetic catechol wastewater and in effectively achieving reduction in TOC, COD and catechol exceeding 81, 88 and better than 99 percent, respectively.

A steady state carbon material balance across the treatment system revealed that almost all the organic carbon removed was converted to methane gas and gaseous and aqueous carbon dioxide.

During the second phase of this experiment which lasted for 178 days, the catechol content of the feed substrate was increased to 400 mg/l resulting in a feed TOC and COD of 255 and 940 mg/l, respectively. The response of the system was an immediate increase in gas production. After a transitional period of 56 days, steady-state operating conditions were reached. Once again, steady-state data served to emphasize that a reactor consisting of one column having an empty bed contact time of 11.62 hours was sufficient in achieving reductions in TOC, COD and catechol exceeding 84, 93 and 99 percent, respectively. At steady-state, 86 percent of the carbon in the feed solution was accounted for indicating that almost all of the organic carbon removed in the process was converted to methane gas and gaseous and aqueous carbon dioxide.

During the third and last phase of this experiment, the performance of the anaerobic activated carbon filter in treating a synthetic wastewater bearing 1000 mg/l of catechol and having a TOC and COD of 758 and 2165 mg/l, respectively, was tested for a period of 47 days. The response of the system was an immediate increase in gas production with no apparent shock effect. The resulting data showed that a reactor consisting of one column having an empty bed contact time of 11.62 hours was sufficient in achieving reductions in TOC, COD and catechol exceeding 94, 94, and 98 percent, respectively.

The treatment of an o-cresol bearing substrate in the second set of anaerobic activated carbon filters was unsuccessful, however. The activated carbon in the filters performed very much like an adsorption column with

the eventual breakthrough of o-cresol occurring in the proximity of what would be predicted from literature isotherm data.

This research has served to illustrate the potential of the anaerobic-activated carbon filter in the treatment of phenolic compounds. Results obtained to date in a parallel study on the treatment of phenol have indicated that this treatment system is also very efficient in reducing the phenolic content of phenol bearing wastewater and in producing a usable end product, methane.

Future research in this area should focus on the treatability of other phenolic compounds by this process. The performance of this novel treatment process in reducing the phenolic content of real industrial wastewaters should also be investigated. It is strongly recommended that a study on the treatment of a real wastewater and a synthetic wastewater, having a phenolic content equivalent to that in the real waste, be conducted so as to establish once and for all, whether or not the use of synthetic wastewaters in the evaluation of process performance is valid.

REFERENCES

1. Ackerman, D. G., et al., "Destroying Chemical Wastes in Commercial Scale Incinerators: Facility Report Number 3, etc...." TRW Defense and Space Systems Group, Redondo Beach, Calif., EPA/SW-122C-3 (April, 1977)
2. Adams, A. D., "Improving Activated Sludge Treatment with Powdered Activated Carbon," Paper presented at the 28th Purdue Industrial Waste Conference, West Lafayette, Indiana.
3. Adams, C. E., "Treatment of a High Strength Phenolic and Ammonia Wastestream by Single and Multi-stage Activated Sludge Processes," Paper presented at the 29th Purdue Industrial Waste Conference, Lafayette, Indiana (1974).
4. Arora, H. C., S. N. Chattopadhyaya and T. Routh, "Treatment of Vegetable Tanning Effluent by the Anaerobic Contact Filter Process," JWPCF, paper submitted for publication, (1975).
5. Besik, F., "High Rate Adsorption-Bio-Oxidation of Domestic Sludge," Water and Sewage Works, 120, 68 (1973).
6. Bishop, D. F., T. P. O'Farrell and J. B. Stamberg, "Physical-Chemical Treatment of Municipal Wastewater," Journal of Water Pollution Control Fed., 44, 3 (Mar. 1972).
7. Buswell, A. M. and F. W. Sollo, Journal of American Chemical Society, 70, 1778 (1948).
8. Capestany, G. J., J. McDaniels and J. L. Opgrande, "The Influence of Sulfate on Biological Treatment of Phenobenzaldehyde Wastes," Jour. Water Poll. Control Fed., 49, 259 (1977).
9. Characklis, W. G., "Attached Microbial Growth," I. Attachment and Growth, Water Research, 2, 1103 (1973).
10. Chian, E. S. K., Y. Chang, F. B. DeWalle and W. B. Rose, "Combined Treatment of an Organic Chemical Water by Activated Sludge Followed by Activated Carbon," Paper presented at the 30th Purdue Industrial Waste Conference, West Lafayette, Indiana.
11. Chian, E. S. K. and F. B. DeWalle, "Treatment of High Strength Acidic Wastewater with a Completely Mixed Anaerobic Filter," Water Research, 11, 294 (1977).
12. Chmielowski, J., A. Grossman and T. Wegrzynowska, "The Anaerobic Decomposition of Phenol During Methane Fermentation," Zesk. Nuak Politech Slask Iniz. Sanit. 8:97-122.

13. Chou, W. L., R. H. Siddiqi, K. McKeon and R. R. Speece, "Methane Production from the Anaerobic Treatment of Petrochemical Wastewaters," Drexel Univ. (1977).
14. Clark, F. M. and L. R. Fina, "The Anaerobic Decomposition of Benzoic Acid During Methane Fermentation," Archives of Biochemistry and Biophysics, 36, 26 (1952).
15. Dagley, S. P., P. J. Chapman, D. T. Gibson and J. M. Wood, "Degradation of the Benzene Nucleus by Bacteria," Nature (London) 202:775 (1964).
16. Dagley, S., W. C. Evans and D. W. Ribbons, "New Pathways in the Oxidative Metabolism of Aromatic Compounds by Microorganisms," Nature (London) 189:560 (1960).
17. Davis, R. W., J. A. Biehl and R. M. Smith, "Pollution Control and Waste Treatment at an Inland Refiner," Paper presented at the 19th Purdue Industrial Waste Conference, Lafayette, Indiana (1964).
18. DeWalle, F. B. and E. S. K. Chian, "Biological Regeneration of Powdered Activated Carbon Added to Activated Sludge Units," Water Research, 11, pp 439-446 (1977).
19. Diehl, D. S., Denbo, R. T., M. N. Bhatla and W. D. Sitman, "Effluent Quality Control at a Large Oil Refiner," Jour. Water Poll. Control Fed., 43:2254 (November 1971).
20. Dutton, P. L. and W. C. Evans, "The Metabolism of Aromatic Compounds by Rhodopseudomonas Palustris: A New, Reductive Method of Aromatic Ring Metabolism," Biochem. Jour., 113:525 (1969).
21. Eckenfelder, W. W., Jr., T. Williams and G. Schlossnagle, "Physical and Chemical Interrelationships in Carbon Adsorption," Paper presented at the Applications of New Concepts of Physical-Chemical Wastewater Treatment, (Sept. 1972).
22. Eisenhauer, H. R., "Oxidation of Phenolic Wastes," Jour. Water Poll. Control Fed., 36:1116 (September 1964).
23. Eisenhauer, H. R., "The Ozonation of Phenolic Wastes," Jour. Water Poll. Control Fed., 40:1887 (1968).
24. El-Shafie, A. T. and D. E. Bloodgood, "Anaerobic Treatment in a Multiple Upflow Filter System," Jour. Water Poll. Control Fed., 45:11, 2345 (November, 1973).
25. Evans, W. C., "The Microbiological Degradation of Aromatic Compounds," Microbiol., 32, 177-184 (1963).
26. Ferguson, J. F., G. F. P. Keay, M. S. Merrill and A. H. Benedict, "Powdered Activated Carbon Biological Treatment: Low Detention Time Process," Paper presented at the 31st Purdue Industrial Waste Conference, West Lafayette, Indiana.

27. Ferrari, A., New York Academy of Science, 87:2,792-800 (July 22, 1960).
28. Ferry, J. G. and R. S. Wolfe, "Anaerobic Degradation of Benzoate to Methane by a Microbial Consortium," Arch. Microbiol., 107:33-40 (1976).
29. Fina, L. R. and A. M. Fiskin, "The Anaerobic Decomposition of Benzoic Acid During Methane Fermentation, II. Fate of Carbons One and Seven," Archives of Biochemistry and Biophysics, 91, 163-165 (1960).
30. Flynn, B. P., F. L. Robertaccio and L. T. Barry, "Truth or Consequences" Biological Fouling and Other Considerations in the Powdered Activated Carbon-Activated Sludge System," Paper presented at the 31st Purdue Industrial Waste Conference, West Lafayette, Indiana.
31. Forney, A. J., W. P. Haynes, S. J. Gasior, G. E. Johnson and J. P. Strakey "Analysis of Tars, Chars, Gases, and Water in Effluents from the Synthane Process," U.S. Bureau of Mines Technical Progress Report 76, Pittsburgh Energy Research Center, Pittsburgh, Pa. (1974).
32. Ganczarczyk, J. and D. Elion, "Extended Aeration of Coke Plant Effluents," Paper presented at the 33rd Purdue Industrial Wastewater Conference, Purdue University, Lafayette, Indiana (1978).
33. Gibson, D. T., J. M. Wood, P. J. Chapman and S. Dagley, "Bacterial Degradation of Aromatic Compounds," Biotech. and Bioengin., 4:33-44 (1967).
34. Gould, J. P. and W. J. Weber, Jr., "Oxidation of Phenols by Ozone," Jour. Water Poll. Control Fed., 48:47 (1976).
35. Guyer, M. and G. Hegeman, "Evidence for a Reductive Pathway for the Anaerobic Metabolism of Benzoate," J. Bacteriol., 99:906 (1969).
36. Hals, O. and A. Benedek, "Simultaneous Biological Treatment and Activated Carbon Adsorption," Paper presented at the 46th Annual Conference of the Water Pollution Control Federation, Cleveland, Ohio (1973).
37. Harary, I., "Bacterial Degradation of Nicotinic Acid," Nature (London) 177:328 (1956).
38. Healy, J., W. Owen, D. Stuckey, L. Y. Young, and P. L. McCarty, "Heat Treatment of Organics for Increasing Anaerobic Biodegradability," Qtr. Progress Report, Dept. of Civil Engineering, Stanford (1977).
39. Healy, J. and L. Y. Young, "Catechol and Phenol Degradation by a Methanogenic Population of Bacteria," Applied and Environ. Microbiol., 35:216-218 (1977).
40. Ho, C. H., B. R. Clark and M. R. Guerin, "Direct Analysis of Organic Compounds in Aqueous By-Products from Fossil Fuel Conversion Processes: Oil Shale Retorting, Synthane Coal Gasification and COED Liquification," Journal Environmental Science Health, A11, 7 (1976).

41. Hopkins, C. B., et al., "Granular Carbon Treatment of Raw Sewage," Washington D.C.: Federal Water Quality Administration (May 1970).
42. Huber, L., "Disposal of Effluents from Petroleum Refineries and Petrochemical Plants," Paper presented at the 22nd Purdue Industrial Waste Conference, Lafayette, Indiana (1967).
43. Hudson, J., doctoral thesis (to be published, 1979).
44. Jennett, J. C. and N. D. Dennis, Jr., "Anaerobic Filter Treatment of Pharmaceutical Waste," Jour. Water Poll. Control Fed., 47:1, 104 (January 1975).
45. Johnson, R. L., "Biological Regeneration of Activated Carbon in Advanced Wastewater Treatment," Lehigh University, Bethlehem, Penn. (June 1975).
46. Kalinski, A. A., "Enhancement of Biological Oxidation of Organic Wastes Using Activated Carbon in Microbial Suspensions," Water Sewage Works, 115 (1972).
47. Klemetson, S. L., "Pollution Potentials of Coal Gasification Plants," (1977).
48. Klotz, M., P. Werner, and R. Schneisfurth, "Investigations Concerning the Microbiology of Activated Carbon Filters," Transcript of Reports in Special Problems of Water Technology, 9-Adsorption (1975).
49. Koppe, P., G. Sebesta and H. Harkelmann, "The Biochemical Oxidation of a Slowly Degradable Substance in the Presence of Activated Carbon: Biocarbon Unit," Gesundheits Ingenieur, 95, 247-248 (1974).
50. Kornegay, B. H. and F. G. Pohland, "The Use of Activated Carbon in Biological Waste Treatment," Presented before the Division of Water, Air and Waste Chemistry, American Chemical Society, Minneapolis, Minnesota (April 1969).
51. Lanouette, K. H., "Treatment of Phenolic Wastes," Chemical Engineering, 99 (1977).
52. Lovan, C. R. and E. G. Foree, "The Anaerobic Filter for the Treatment of Brewery Press Liquor Waste," Presented at the 26th Purdue Industrial Waste Conference, West Lafayette, Indiana.
53. Lundgren, D. P., "Phosphate Analysis with the Technicon Auto Analyzer," Analytical Chemistry, 32:824 (June 1960).
54. Mazur, M., "Biological Purification of Spent Phenolic Waters from the Hunedoara Coking Plant," Metalurgia (Bucharest), 26: No. 4, 227 (1974).
55. Maqsood, R. and A. Benedek, "Low-Temperature Organic Removal and Denitrification in Activated Carbon Columns," Journal of Water Pollution Control Fed., 2107-2117 (Oct. 1977).

56. McCarty, P. L., "Anaerobic Waste Treatment Fundamentals. Part One: Chemistry and Microbiology," Public Works, 107 (September 1964).
57. McCarty, P. L., "Anaerobic Treatment of Soluble Wastes," presented at the Special Lecture Series on Advances in Water Quality Improvement, the University of Texas (April 4-7, 1966).
58. McKinney, R., H. Tomlinson and R. Wilcox, "Metabolism of Aromatic Compounds by Activated Sludge," Sewage and Industrial Wastes, 28, 547 (1956).
59. Miller, G. W. and R. G. Rice, "European Water Treatment Practices-The Promise of Biological Activated Carbon," Civil Engineering-ASCE, 81 (Feb.1978).
60. Miller, T. L. and M. J. Wolin, "A Serum Bottle Modification of the Hungate Technique for Cultivating Obligate Anaerobes," Applied Microbiology, 27:5, 985-987 (May 1974).
61. Mueller, J. C., J. M. Leach and C. C. Walden, "Detoxification of Bleached Kraft Mill Effluents-A Manageable Problem," Paper presented at the 1977 Tappi Environmental Conference, Chicago, Illinois (1977).
62. Mueller, J. A. and J. L. Mancini, "Anaerobic Filter-Kinetics and Application," presented at the 30th Purdue Industrial Waste Conference, West Lafayette, Indiana.
63. Nebel, C., R. D. Gottschling, J. L. Holmes and P. C. Unangst, "Ozone Oxidation of Phenolic Effluents," Welsbach Ozone System Corp. (1976).
64. Nemerow, N. L., Industrial Water Pollution: Origins, Characteristics, and Treatment, Addison-Wesley Publishing Company (1978).
65. Niegowski, S. J., "Destruction of Phenols by Oxidation with Ozone," Industrial and Engineering Chemistry, 45:632 (1953).
66. Norrman, J. and B. Frostell, "Anaerobic Waste Water Treatment in a Two-Stage Reactor of a New Design," presented at the 32nd Purdue Industrial Waste Conference, West Lafayette, Indiana.
67. Nottingham, P. M. and R. E. Hungate, "Methanogenic Fermentation of Benzoate," Jour. of Bact., 98:3, 1170-1172 (1969).
68. Oshima, T., "On the Anaerobic Metabolism of Aromatic Compounds in the Presence of Nitrate by a Soil Microorganism," Z. Allg. Mikrobiol., 5:386-394 (1965).
69. Pafford, R. J., Jr., P. DeFalco, Jr. and J. R. Teerink, "Denitrification by Anaerobic Filters and Ponds Phase II," Water Pollution Control Research Series, 13030 Ely 06/71-14 (June 1971).
70. Parkhurst, J. D., F. D. Dryden, G. N. McDermott and J. English, "Pomona Activated Carbon Pilot Plant," Jour. Water Poll. Control Fed., 39, 10:2 (Oct. 1967).

71. Perrotti, A. E. and C. A. Rodman, "Factors Involved with Biological Regeneration of Activated Carbon," AIChE Symposium Series, 70, 144 (1974).
72. Plummer, A. H., Jr., J. F. Malina, Jr., and W. W. Eckenfelder, Jr., "Stabilization of a Low Solids Carbohydrate Waste by an Anaerobic Submerged Filter," presented at the 23rd Purdue Industrial Waste Conference, West Lafayette, Indiana.
73. Rice, R. G., C. Gomella and G. W. Miller, "Rouen, France Water-Treatment Plant: Good Organics and Ammonia Removal with No Need to Regenerate Carbon Beds," ASCE, 48, 5 (May 1978).
74. Rizzo, J. L. and R. E. Schade, "Secondary Treatment with Granular Activated Carbon," Water and Sewage Works, 116, pp 307-312 (1969).
75. Roberts, F. F., M. S. Thesis, Kansas State Univ., (1962).
76. Rodman, G. A. and E. L. Shunney, "Bio-Regenerated Activated Carbon Treatment of Textile Dye Wastewaters," Water Pollution Control Research Series: EPA (Jan. 1975).
77. Rosfjord, R. E., "Phenols: A Water Pollution Control Assessment," Water and Sewage Works (1975).
78. Rudolfs, W. and E. H. Trubnick, "Activated Carbon in Sewage Treatment," Sewage Works Journal, 7, 5 (Sept. 1935).
79. Sack, W. A. and W. R. Bokey, "Biological Treatment of Coal Gasification Wastewater," Paper presented at the 33rd Purdue Industrial Waste Conference, Lafayette, Indiana (1978).
80. Sachs, E. F., J. C. Jennett and M. C. Rand, "Anaerobic Treatment of Synthesized Organic Chemical Pharmaceutical Wastes," Presented at the 33rd Purdue Industrial Waste Conference, West Lafayette, Indiana.
81. Sauders, W. M., "Oxygen Utilization by Slime Organisms in Continuous Cultures," International Journal of Air and Water Pollution, 10, 253 (1968).
82. Scaramelli, A. B. and F. A. DiGiano, "Upgrading the Activated Sludge System by Addition of Powdered Activated Carbon," Water Sewage Works, 120, 90-94 (1970).
83. Schmidt, C. E., A. G. Sharkey, and R. A. Friedel, "Mass Spectrometric Analysis of Product Water from Coal Gasification," U.S. Bureau of Mines Technical Progress Report 86, Pittsburgh Energy Research Center, Pittsburgh, Pa. (1974).
84. Shell, G. L. and D. E. Burns, "Powdered Activated Carbon Application, Regeneration, and Reuse in Wastewater Treatment Systems," Proceedings of the 6th International Conference held in Jerusalem (June 1972).

85. Simpson, F. S., G. A. Jones and E. A. Wolin, "Anaerobic Degradation of Some Bioflavanoids by Microflora of the Rumen," Cand. J. of Microbiol., 15:972 (1969).
86. Singer, P. C., F. K. Pfaender, J. Chinchilli and J. C. Lamb, III, "Composition and Biodegradability of Organics in Coal Conversion Wastewaters," Paper presented at the 3rd Symposium on Environmental Aspects of Fuel Conversion Technology (1977).
87. Spencer, R. R., "The Addition of Powdered Activated Carbon to Anaerobic Digesters: Effects on Methane Production," Master's Thesis, Univ. of Washington, (1976).
88. Stadtman, T. C. and H. A. Barker, "Studies on the Methane Fermentation, VII Tracer Experiments in the Mechanism of Methane Formation," Archives Biochem., 21, 256 (1949).
89. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th edition (1975).
90. Stanier, R. Y., "The Oxidation of Aromatic Compounds by Fluorescent Pseudomonads," J. Bacteriol., 55:477-494 (1948).
91. Stenstrom, M. K. and C. C. Grieves, "Enhancement of Oil Refinery Activated Sludge by Addition of Powdered Activated Carbon," Paper presented at the 32nd Purdue Industrial Waste Conference, West Lafayette, Indiana.
92. Tamblyn, T. A. and B. R. Sword, "The Anaerobic Filter for the Denitri-fication of Agricultural Subsurface Drainage," Presented at the 24th Purdue Industrial Waste Conference, West Lafayette, Indiana.
93. Tarvin, D. and A. M. Buswell, "The Methane Fermentation of Organic Acids and Carbohydrates," Journal of American Chemical Society, 56, 1751 (1934).
94. Taylor, D. W., "Full-Scale Anaerobic Trickling Filter Evaluation," Proceedings of the 3rd National Symposium on Food Processing Waste, EPA Technology Transfer EPA-R2-018 (1972).
95. Taylor, B. F., W. L. Campbell, and I. Chinoy, "Anaerobic Degradation of the Benzene Nucleus by a Facultative Anaerobic Microorganism," J. Bacteriol., 102:430-437 (1970).
96. "Technicon AutoAnalyzer Methodology: Ammonia in Water and Wastewater," Industrial Method In.-19-69W.
97. "Technicon AutoAnalyzer Methodology: Total Inorganic Phosphate in Water and Waste Water," Industrial Method 4-68W.
98. "Technicon AutoAnalyzer Methodology: Total Nitrogen (Kjeldahl)," Industrial Method 30-69A.

99. Tofflemire, T. J., L. J. Hetling and W. W. Shuster, "Activated Carbon Adsorption and Polishing of Strong Wastewater," Jour. Water Poll. Control Fed., 45, 10 (Oct. 1973).
100. Tsai, C. and G. A. Jones, "Isolation and Identification of Rumen Bacteria Capable of Anaerobic Phloroglucinol Degradation," Can. J. Microbiol., 21:794 (1975).
101. Volkova, L. I., "Chemical Composition and Methods for Purifying Phenolic Waste Waters Resulting from Rapid Thermolysis of Lignites of the Irsha-Borodino and Moscow Regions,"
102. Wabers, B. A., "Removal of Wood-derived Toxic Compounds from Pulp and Paper Mill Effluents by Waste Treatment Processes," Paper presented at the 1978 TAPPI Environmental Conference, Washington, D.C., (1978).
103. Wallace, R. N. and D.E. Burns, "Factors Affecting Powdered Carbon Treatment of a Municipal Wastewater," Jour. Water Poll. Control Fed., 48, 3 (March 1976).
104. Weber, W. J., Jr., "Discussion: Biological Fluidized-bed Treatment for BOD and Nitrogen Removal," Jour. Water Poll. Control Fed., (April 1978).
105. Weber, W. J., Jr., "Integrated Biological and Physico-Chemical Treatment for Reclamation of Wastewater," Industrial Waste Engineering, (Dec. 1971).
106. Weber, W. J., Jr., Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York (1972).
107. Weber, W. J., Jr., L. D. Friedman and R. Bloom, Jr., "Biologically-Extended Physicochemical Treatment," Proceedings of the 6th International Conference held in Jerusalem (June 1972).
108. Williams, R. J. and W. C. Evans, "Anaerobic Metabolism of Aromatic Substrates by Certain Microorganisms," Biochem. Soc. Trans., 1:186 (1973).
109. Williams, R. J. and W. C. Evans, "The Metabolism of Benzoate by Moraxella Species Through Anaerobic Nitrate Respiration: Evidence for a Reductive Pathway," Biochem J., 148:1-10 (1975).
110. Witt, E. R., W. J. Humphrey and T. E. Roberts, "Full-Scale Anaerobic Filter Treats High Strength Wastes," Paper presented at 1979 Purdue University Industrial Waste Conference, West Lafayette, Indiana (1979).
111. Wurm, H. J., "The Treatment of Phenolic Wastes," Paper presented at the 23rd Purdue Industrial Waste Conference, Lafayette, Indiana (1968).
112. Young, J. C. and P. L. McCarty, "The Anaerobic Filter for Waste Treatment," Presented at the 22nd Purdue Industrial Waste Conference, West Lafayette, Indiana.
113. Young, J. C. and P. L. McCarty, "The Anaerobic Filter for Waste Treatment," Doctoral Thesis (March 1968).

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